

# EPA/NSF ETV PROTOCOL

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## PROTOCOL FOR EQUIPMENT VERIFICATION TESTING FOR THE REMOVAL OF SYNTHETIC ORGANIC CHEMICAL CONTAMINANTS



**EPA/NSF ETV  
PROTOCOL FOR EQUIPMENT VERIFICATION TESTING  
FOR THE REMOVAL OF SYNTHETIC ORGANIC  
CHEMICAL CONTAMINANTS  
November 12, 1999**

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Recommended by  
the Steering Committee for the Verification of  
Package Drinking Water Treatment Systems/Plants  
on August 2, 1999

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## **NSF INTERNATIONAL**

### **Mission Statement:**

NSF International (NSF), an independent, not-for-profit organization, is dedicated to public health safety and protection of the environment by developing standards, by providing education and providing superior third party conformity assessment services while representing the interests of all stakeholders.

### **NSF Purpose and Organization**

NSF International (NSF) is an independent not-for-profit organization. For more than 52 years, NSF has been in the business of developing consensus standards that promote and protect public health and the environment and providing testing and certification services to ensure manufacturers and users alike that products meet those standards. Today, millions of products bear the NSF Name, Logo and/or Mark, symbols upon which the public can rely for assurance that equipment and products meet strict public health and performance criteria and standards.

### **Limitations of use of NSF Documents**

This protocol is subject to revision; contact NSF to confirm this revision is current. The testing against this protocol does not constitute an NSF Certification of the product tested.

## **U.S. ENVIRONMENTAL PROTECTION AGENCY**

Throughout its history, the U.S. Environmental Protection Agency (EPA) has evaluated technologies to determine their effectiveness in preventing, controlling, and cleaning up pollution. EPA is now expanding these efforts by instituting a new program, the Environmental Technology Verification Program---or ETV---to verify the performance of a larger universe of innovative technical solutions to problems that threaten human health or the environment. ETV was created to substantially accelerate the entrance of new environmental technologies into the domestic and international marketplace. It supplies technology buyers and developers, consulting engineers, states, and U.S. EPA regions with high quality data on the performance of new technologies. This encourages more rapid availability of approaches to better protect the environment.

### **ETV's Package Drinking Water Treatment Systems Pilot Project:**

Concern about drinking water safety has accelerated in recent years due to much publicized outbreaks of waterborne disease and information linking ingestion of high levels of disinfection byproducts to cancer incidence. The U.S. EPA is authorized through the Safe Drinking Water Act to set numerical contaminant standards and treatment and monitoring requirements that will ensure the safety of public water supplies. However, small communities are often poorly equipped to comply with all of the requirements; less costly package treatment technologies may offer a solution. These package plants can be designed to deal with specific problems of a particular community; additionally, they may be installed on site more efficiently---requiring less start-up capital and time than traditionally constructed water treatment plants. The opportunity for the sales of such systems in other countries is also substantial.

The U.S. Environmental Protection Agency (EPA) has partnered with NSF, a nonprofit testing and certification organization, to verify performance of small package drinking water systems that serve small communities. It is expected that both the domestic and international markets for such systems are substantial. EPA and NSF have formed an oversight stakeholders group composed of buyers, sellers, and states (issuers of permits), to assist in formulating consensus testing protocols. A goal of verification testing is to enhance and facilitate the acceptance of small package drinking water treatment equipment by state drinking water regulatory officials and consulting engineers while reducing the need for testing of equipment at each location where the equipment use is contemplated. NSF will meet this goal by working with equipment Manufacturers and other agencies in planning and conducting equipment verification testing, evaluating data generated by such testing and managing and disseminating information. The Manufacturer is expected to secure the appropriate resources to support their part of the equipment verification process, including provision of equipment and technical support.

The verification process established by EPA and NSF is intended to serve as a template for conducting water treatment verification tests that will generate high quality data for verification of equipment performance. The verification process is a model process that can help in moving small package drinking water equipment into routine use more quickly. The verification of an equipment's performance involves five sequential steps:

1. Development of a verification/Field Operations Document;
2. Execution of verification testing;
3. Data reduction, analysis, and reporting;
4. Performance and cost (labor, chemicals, energy) verification;
5. Report preparation and information transfer.

This verification testing program is being conducted by NSF International with participation of manufacturers, under the sponsorship of the EPA Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division (WSWRD) - Cincinnati, Ohio. NSF's role is to provide technical and administrative leadership and support in conducting the testing. It is important to note that verification of the equipment does not mean that the equipment is "certified" by NSF or EPA. Rather, it recognizes that the performance of the equipment has been determined and verified by these organizations.

#### **Partnerships:**

The U.S. EPA and NSF International (NSF) are cooperatively organizing and developing the ETV's Package Drinking Water Treatment Systems Pilot Project to meet community and commercial needs. NSF and the Association of State Drinking Water Administrators have an understanding to assist each other in promoting and communicating the benefits and results of the project.

## **ORGANIZATION AND INTENDED USE OF PROTOCOL AND TEST PLANS**

NSF encourages the user of this protocol to also read and understand the policies related to the verification and testing of package drinking water treatment systems and equipment.

The first Chapter of this document describes the Protocol required in all studies verifying the performance of equipment or systems removing synthetic organic chemical contaminants, the public health goal of the Protocol. The remaining chapters describe the additional requirements for equipment and systems using specific technologies to attain the goals and objectives of the Protocol: the removal of synthetic organic chemical contaminants.

Prior to the verification testing of a package drinking water treatment systems, plants and/or equipment, the equipment manufacturer and/or supplier must select an NSF-qualified, Field Testing Organization. This designated Field testing Organization must write a “Field Operations Document” (FOD). The equipment manufacturer and/or supplier will need this protocol and the test plans herein and other NSF Protocols and Test Plans to develop the Field Operations Document depending on the treatment technologies used in the unit processes or treatment train of the equipment or system. More than one protocol and/or test plan may be necessary to address the equipment’s capabilities in the treatment of drinking water.

Testing shall be conducted by an NSF-qualified, Field Testing Organization that is selected by the Manufacturer. Water quality analytical work to be completed as a part of an NSF Equipment Verification Testing Plan shall be contracted with a state-certified or third party- or EPA-qualified laboratory. For information on a listing of NSF-qualified field testing organizations and qualified laboratories, contact NSF International.

## TABLE OF CONTENTS

	<u>Page</u>
<b>Chapter 1: EPA/NSF ETV Protocol for Equipment Verification Testing for the Removal of Synthetic Organic Chemical Contaminants: Requirements for All Studies.....</b>	<b>1-1</b>
<b>Chapter 2: EPA/NSF ETV Equipment Verification Testing Plan for the Removal of Synthetic Organic Chemical Contaminants by Membrane Filtration Processes.....</b>	<b>2-1</b>
<b>Chapter 3: EPA/NSF ETV Equipment Verification Testing Plan for SOC Oxidation by Ozone and Advanced Oxidation Processes .....</b>	<b>3-1</b>
<b>Chapter 4: Reserved – EPA/NSF ETV Equipment Verification Testing Plan – Adsorptive Media for the Removal of SOC's .....</b>	<b>4-1</b>

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**CHAPTER 1**

**EPA/NSF ETV**

**PROTOCOL FOR EQUIPMENT VERIFICATION TESTING**

**FOR THE REMOVAL OF**

**SYNTHETICORGANIC CHEMICAL CONTAMINANTS**

**REQUIREMENTS FOR ALL STUDIES**

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## TABLE OF CONTENTS

	<u>Page</u>
<b>LIST OF ABBREVIATIONS</b> .....	1-4
<b>1.0 INTRODUCTION</b> .....	1-5
1.1 Objectives.....	1-7
1.2 Scope .....	1-8
<b>2.0 EQUIPMENT VERIFICATION TESTING RESPONSIBILITIES</b> .....	1-9
2.1 Verification Testing Organization and Participants .....	1-9
2.2 Organization.....	1-9
2.3 Verification Testing Site Name and Location .....	1-10
2.4 Site Characteristics.....	1-10
2.5 Responsibilities .....	1-10
<b>3.0 EQUIPMENT CAPABILITIES AND DESCRIPTION</b> .....	1-11
3.1 Equipment Capabilities .....	1-11
3.2 Equipment Description.....	1-14
<b>4.0 EXPERIMENTAL DESIGN</b> .....	1-15
4.1 Objectives.....	1-15
4.2 Equipment Characteristics.....	1-16
4.2.1 Qualitative Factors .....	1-16
4.2.2 Quantitative Factors .....	1-17
4.3 Water Quality Considerations .....	1-17
4.3.1 Feed Water Quality .....	1-18
4.3.2 Treated Water Quality .....	1-18
4.4 Synthetic Organic Chemical Contaminants Testing.....	1-19
4.5 Recording Data.....	1-19
4.6 Recording Statistical Uncertainty.....	1-19
4.7 Verification Testing Schedule .....	1-20
<b>5.0 FIELD OPERATIONS PROCEDURES</b> .....	1-22
5.1 Equipment Operations and Design.....	1-22
5.2 Selection of Analytical Laboratory and Field Testing Organization.....	1-22
5.3 Communications, Documentation, Logistics, and Equipment .....	1-23
5.4 Initial Operations.....	1-23
5.5 Equipment Operation and Water Quality Sampling for Verification Testing....	1-24

## TABLE OF CONTENTS (continued)

	<b><u>Page</u></b>
<b>6.0 QUALITY ASSURANCE PROJECT PLAN</b> .....	1-24
6.1 Purpose and Scope .....	1-25
6.2 Quality Assurance Responsibilities .....	1-25
6.3 Data Quality Indictors .....	1-25
6.3.1 Accuracy .....	1-26
6.3.2 Precision .....	1-27
6.3.3 Representativeness .....	1-27
6.3.4 Statistical Uncertainty .....	1-28
6.4 Water Quality and Operational Control Checks .....	1-28
6.4.1 Quality Control for Equipment Operation .....	1-28
6.4.2 Water Quality Data .....	1-29
6.4.2.1 Duplicate Analysis of Selected Water Quality Parameters .....	1-29
6.4.2.2 Method Blanks .....	1-29
6.4.2.3 Spiked Samples .....	1-29
6.4.2.4 Travel Blanks .....	1-29
6.4.2.5 Performance Evaluation Samples for On-Site Water Quality Testing ...	1-29
6.5 Data Reduction, Validation, and Reporting .....	1-30
6.5.1 Data Reduction .....	1-30
6.5.2 Data Validation .....	1-30
6.5.3 Data Reporting .....	1-30
6.6 System Inspections .....	1-31
6.7 Reports .....	1-31
6.7.1 Status Reports .....	1-31
6.7.2 Inspection Reports .....	1-31
6.8 Corrective Action .....	1-31
 <b>7.0 DATA MANAGEMENT, ANALYSIS AND REPORTING</b> .....	 1-32
7.1 Data Management and Analysis .....	1-32
7.2 Report of Equipment Testing .....	1-33
 <b>8.0 SAFETY AND MAINTENANCE CONSIDERATIONS</b> .....	 1-34

## TABLE

Table 3.1	Example Statements of Performance Capabilities for SOC Removal .....	1-12
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## LIST OF ABBREVIATIONS

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DOC	dissolved organic carbon
EPA	United States Environmental Protection Agency
ETV	Environmental Technology Verification
FOD	Field Operations Document
gsfd	gallons per square foot day
MCL	Maximum Contaminant Level
mg/L	milligrams per liter
NPDOC	non-purgeable dissolved organic carbon
NSF	NSF International
PE	performance evaluation
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
rpm	revolutions per minute
percent	percent relative standard deviation
RSD	
SDWA	Safe Drinking Water Act
SOC	synthetic organic contaminant
TDS	total dissolved solids
TOC	total organic carbon
µg/L	micrograms per liter
UV-254	ultraviolet absorbance @ 254 wavelength
WSWRD	Water Supply and Water Resources Division

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## 1.0 INTRODUCTION

This document is the study protocol that will be used for Verification Testing of equipment designed to achieve removal of synthetic organic chemical contaminants (SOCs). This protocol may be applicable to various types of water treatment equipment capable removal of SOCs. Equipment testing may be undertaken to verify performance of a packaged plant systems employing processes that may include but are not limited to coagulation/clarification, oxidation or mixed oxidation processes, adsorption, granular activated carbon biological filtration, encapsulation, and/or membrane processes for removal of SOCs. The specific SOC to be targeted for removal during Verification Testing shall be clearly identified in the Field Operations Document (FOD) prior to the initiation of testing by the Field Testing Organization (FTO). The FOD may include more than one Testing Plan; however, the FTO must adhere to the specific minimum requirements of each study protocol in developing a FOD.

The testing of new technologies and materials that are unfamiliar to the NSF/EPA will not be discouraged. It is recommended that resins or membranes or any other material or chemical in the package plant conform to American National Standards Institute/NSF International (ANSI/NSF) Standard 60 and 61.

The final submission of the FOD shall:

- Include the information requested in this protocol.
- Conform to the format identified in this protocol.
- Conform to the specific NSF International (NSF) Equipment Verification Testing Plan or Plans related to the Statement or Statements of capabilities that are to be verified.

This protocol document is presented in two fonts. The non-italicized font provides the rationale for the requirements and background information that the FTO may find useful in preparation of the FOD. *The italicized text indicates specific study protocol deliverables that are required of the FTO or the Manufacturer and that must be incorporated in the FOD.*

The following glossary terms are presented here for subsequent reference in this protocol:

- **Company** - Any public or private organization, group, individual, or other entity contracting with NSF, or a subsidiary or division of such an entity.
- **Distribution System** - A system of conduits by which a primary water supply is conveyed to consumers, typically by a network of pipelines.
- **EPA** - The United States Environmental Protection Agency, its staff or authorized representatives.
- **Equipment** - Testing equipment for use in the Verification Testing Program, which may be defined as either a package plant or modular system.
- **Field Operations Document (FOD)** - A written document of procedures for on-site/in-line testing, sample collection, preservation, and shipment and other on-site activities described in the EPA/NSF Protocol(s) and Test Plan(s) that apply to a specific make and model of a package plant/modular system.

- **Field Testing Organization (FTO)** - An organization qualified to conduct studies and testing of package plants or modular systems in accordance with protocols and test plans. The role of the FTO is to complete the application on behalf of the Company; to enter into contracts with NSF, as discussed herein; arrange for or conduct the skilled operation of a package plant during the intense periods of testing during the study and the tasks required by the Protocol.
- **Manufacturer** - A business that assembles and/or sells package plant equipment and/or modular systems. The role of the Manufacturer is to provide the package plant and/or modular system and technical support during the Verification Testing Program. The Manufacturer is also responsible for providing assistance to the third party FTO during operation and monitoring of the package plant or modular system during the Verification Testing Program.
- **Modular System** - A packaged functional assembly of components for use in a drinking water treatment system or packaged plant that provides a limited form of treatment of the feedwater(s) and which is discharged to another packaged plant or the final step of treatment to the distribution system.
- **NSF** - NSF International, its staff, or other authorized representatives.
- **Package Plant** - A complete water treatment system including all components from the connection to the raw water(s) intake through discharge to the distribution system.
- **Plant Operator** - The person working for a small water system who is responsible for operating package water treatment equipment to produce treated drinking water. This person may also collect samples, record data and attend to the daily operations of equipment throughout the testing periods.
- **Preferred Qualified Field Testing Organization** - One meeting all required qualifications, meeting at least one of the secondary qualifications, and meeting ANSI/ASQC E4-1994 or having a plan to meet ANSI/ASQC E4-1994 within six months.
- **Protocol** - A written document that clearly states the objectives, goals and scope of the study as well as the test plan(s) for the conduct of the study. The protocol shall be used for reference during Manufacturer participation in the Verification Testing Program.
- **Provisionally Qualified Field Testing Organization** - One having identified deficiencies, but demonstrates its ability to conduct valid Verification Testing of package plants and modular systems.
- **Qualified Field Testing Organization** - One meeting all applicable NSF requirements.
- **Report** - A written document that includes data, test results, findings, and any pertinent information collected in accordance with a protocol, analytical methods, procedures etc., in the assessment of a product whether such information is in preliminary, draft or final form.
- **Testing Laboratory** - An organization certified by a third- party independent organization, Federal agency, or a pertinent State regulatory authority to perform the testing of drinking water samples. The role of the testing laboratory in the Verification Testing of package plants and/or modular systems is to analyze the water samples in

accordance with the methods and meet the pertinent quality assurance and quality control requirements described in the protocol, test plan FOD.

- **Testing Plan** - A written document that describes the procedures for conducting a test or study for the application of water treatment technology. At a minimum, the test plan will include detailed instructions for sample and data collection, sample handling and sample preservation, precision, accuracy, and reproducibility goals, and quality assurance and quality control requirements.
- **Verification** - To establish the evidence on the range of performance of equipment and/or device under specific conditions following a predetermined study protocol(s) and test plan(s).
- **Verification Statement** - A written document that summarizes a final report reviewed and approved by NSF on behalf of the EPA or directly by the EPA.
- **Water System** - The water system that operates using packaged water treatment equipment to provide potable water to its customers.

## 1.1 Objectives

The specific objectives of the Equipment Verification Testing Project may be different for each package plant or modular system, depending upon the Statement of Capabilities of the specific equipment to be tested. The objectives developed by each Manufacturer will be defined and described in detail in the FOD developed for each piece of equipment. The objectives of the Equipment Verification Testing Project may include but are not limited to the following:

- Generation of field data appropriate for verifying the performance of the equipment.
- Generation of field data in support of meeting current National Primary Drinking Water Standards, the EPA National Secondary Drinking Water Standards, and/or anticipated water quality regulations. (Note that compliance with Drinking Water Standards or regulations is not necessarily a primary objective of equipment Verification Testing.)
- Generation of operation and maintenance information to assist users and potential operators of equipment.
- Evaluation of new advances in equipment and equipment design.

An important aspect in the development of Verification Testing is to describe the procedures that will be used to verify the Statement of Performance Capabilities made for water treatment equipment. A Verification Testing plan document shall incorporate the quality assurance/quality control (QA/QC) elements needed to provide data of appropriate quality sufficient to reach a defensible position regarding the equipment performance. Although Verification Testing conducted at a single site may not represent every environmental situation, which may be acceptable for the equipment tested, it will provide data of sufficient quality to make a judgment about the application of the equipment under conditions similar to those encountered in the Verification Testing. A Quality Assurance Project Plan (QAPP) shall be described in detail and provided as part of the FOD.

It is important to note that verification of the equipment does not mean that the equipment is “certified” by NSF or EPA. Rather, it recognizes that the performance of the equipment has been determined and verified by these organizations.

## 1.2 Scope

This protocol outlines the verification process for equipment designed to achieve removal of SOC<sub>s</sub>. This protocol can be used in conjunction with a number of different testing plans for packaged and/or modular drinking water treatment systems designed to achieve removal of SOC<sub>s</sub>. This protocol is not an NSF or third-party consensus standard and it does not endorse the packaged plants or technologies described herein.

An overview of the equipment verification process and the elements of the FOD to be developed by the Manufacturer are described in this protocol document. Specifically, the FOD shall define the following elements of the Verification Testing:

- Roles and responsibilities of Verification Testing participants.
- Procedures governing Verification Testing activities such as: equipment operation and process monitoring; sample collection, preservation, and analysis; and data collection and interpretation.
- Experimental design of the Field Operations Procedures. The Field Operations Procedures will identify recommended equipment maintenance and cleaning methods.
- Quality assurance (QA) and quality control (QC) procedures for conducting the Verification Testing and for assessing the quality of the data generated from the Verification Testing.
- Health and safety measures relating to biohazard, electrical, mechanical and other safety codes.

### *Content of FOD Regarding Verification Testing Objectives and Scope*

*The structure of the FOD must conform to the outline below: The required components of the Document will be described in greater detail in the sections below.*

- *TITLE PAGE*
- *FOREWORD*
- *TABLE OF CONTENTS* – *The Table of Contents for the FOD should include the headings provided in this document although they may be modified as appropriate for a particular type of equipment to be tested.*
- *LIST OF DEFINITIONS* - *A list of key terms used in the FOD should be provided*
- *EXECUTIVE SUMMARY* - *The Executive Summary describes the contents of the FOD (not to exceed two pages). A general description of the equipment and the Statement of Performance Capabilities which will be verified during testing as well as the testing locations, a schedule, and a list of participants.*

- *ABBREVIATIONS AND ACRONYMS – A list of the abbreviations and acronyms used in the FOD should be provided.*
- *EQUIPMENT VERIFICATION TESTING RESPONSIBILITIES(Section 2)*
- *EQUIPMENT CAPABILITIES AND DESCRIPTION (Section 3)*
- *EXPERIMENTAL DESIGN (Section 4)*
- *FIELD OPERATIONS PROCEDURES (Section 5)*
- *QUALITY ASSURANCE TESTING PLAN (Section 6)*
- *DATA MANAGEMENT AND ANALYSIS (Section 7)*
- *SAFETY PLAN (Section 8)*

## **2.0 EQUIPMENT VERIFICATION TESTING RESPONSIBILITIES**

### **2.1 Verification Testing Organization and Participants**

This Verification Testing Project is being conducted by NSF International with participation of Manufacturers, under the sponsorship of the EPA Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division (WSWRD) - Cincinnati, Ohio. The WSWRD and NSF jointly are administering the Equipment Verification Testing Program. NSF's role is to provide technical and administrative leadership and support in conducting the testing.

The required content of the FOD and the responsibilities of participants are listed at the end of each section. In the development of a FOD, Manufacturers and their designated FTO shall provide a table including:

- the name, affiliation, and mailing address of each participant;
- a point of contact;
- description of participant's role;
- telephone and fax numbers; and
- e-mail address.

The equipment provided by the Manufacturer shall explicitly meet all requirements of Occupational Safety and Health Association (OSHA), NEMA, Underwriters Laboratory (UL), NSF and other appropriate agencies in order to ensure operator safety during Verification Testing.

### **2.2 Organization**

The organizational structure for the Verification Testing showing lines of communications shall be provided by the FTO in its application on behalf of the Manufacturer.



## **2.3 Verification Testing Site Name and Location**

This section discusses background information on the Verification Testing site(s), with emphasis on the quality of the feedwater, which in some cases may be the source water at the site. The FOD must provide the site names and locations at which the equipment will be tested. In most cases, the equipment will be demonstrated at more than one site. Depending upon the Verification Testing requirements stipulated in the Testing Plan employed, testing of the equipment may be required under different conditions of feedwater quality (or source water quality) that allow evaluation of system performance over a range of seasonal climate and weather conditions.

## **2.4 Site Characteristics**

The FOD shall include an area location map showing access from major streets and highways and a site layout drawing with equipment footprints and dimensions. The drawing should indicate the location of existing facilities, the source of the feed water, and where the treated water will be discharged and the waste streams disposed. Indicate if any facilities other than the package plant would be required such as additional trailers or temporary structures for sample collection and preparation, electrical power, concrete pads, drainage, easements, etc. The location of SOC waste treatment, disposal and discharge facility or method of removal shall be clearly identified in the site plan. The FOD must include a description of the test site. This shall include a description of where the equipment will be located. If the feed water to the packaged plant equipment is the source water for an existing water treatment plant, describe:

- the raw water intake;
- the opportunity to obtain raw water without the addition of any chemicals; and
- the operational pattern of raw water pumping at the full-scale facility (is it continuous or intermittent?).

The source water characteristics shall be described and documented. The FOD shall also describe facilities to be used for handling the treated water and wastes (i.e., residuals) produced during the Verification Testing Program. The FOD will state whether the required water flows and waste flows produced are dealt with in an acceptable way, and whether any water pollution discharge permits are needed.

## **2.5 Responsibilities**

The FOD shall identify the organizations involved in the testing and describes the primary responsibilities of each organization. Multiple Manufacturer testing for removal of SOC's may be conducted concurrently, and be fully in compliance with the NSF Equipment Verification Testing Program. The responsibilities of the Manufacturer will vary depending on the type of Verification Testing. However, at a minimum, the Manufacturer shall be responsible for:

- Providing the equipment to be evaluated during Verification Testing. The equipment must be in complete working order at delivery to the test site.
- Providing logistical and technical support, as required.

- Providing equipment that explicitly meets all requirements of OSHA, NEMA, UL, NSF and other appropriate agencies in order to ensure operator safety during Verification Testing.

The FTO shall be responsible for:

- Providing needed logistical support, establishing a communication network, and scheduling and coordinating the activities of all Verification Testing participants.
- Advising the Manufacturer on feedwater quality and test site selection, such that the locations selected as test sites have feedwater quality consistent with the objectives of the Verification Testing (the Manufacturer may recommend a site for Verification Testing.)
- Managing, evaluating, interpreting, and reporting on data generated by the Verification Testing.
- Evaluating and reporting on the performance of the technologies applied to achieve removal of SOC<sub>s</sub>.

#### ***Content of FOD Regarding Equipment Verification Testing Responsibilities:***

*The Manufacturer shall be responsible for:*

- *Provision of complete, field-ready equipment for Verification Testing.*
- *Provision of logistical and technical support, as required.*
- *Provision of technical assistance to the qualified testing organization during operation and monitoring of the equipment undergoing Verification Testing.*

*The FTO shall be responsible for including the following elements in the FOD:*

- *Definition of the roles and responsibilities of appropriate Verification Testing participants.*
- *A table, which includes the name, affiliation, and mailing address of each participant, a point-of-contact, their role, telephone and fax numbers, and e-mail address.*
- *Organization of operational and analytical support.*
- *List of the site name(s) and location(s).*
- *Description of the test site(s), the site characteristics and identification of where the equipment will be located.*

### **3.0 EQUIPMENT CAPABILITIES AND DESCRIPTION**

#### **3.1 Equipment Capabilities**

For this Verification Testing, the Manufacturer and their designated FTO shall identify in a Statement of Performance Capabilities the specific performance criteria to be verified and the

specific operational conditions under which the Verification Testing shall be performed. In conjunction with a Statement of Performance Capabilities, the FTO shall state the pertinent detection limits for the specific analytical method. Statements should be made regarding the applications of the equipment, the known limitations of the equipment and under what conditions the equipment is likely to fail or underperform. The FTO on behalf of the Manufacturer shall also provide information as to what advantages the Verification Testing equipment provides over existing equipment. The Statement of Performance Capabilities must be specified and verifiable by a statistical analysis of the data. There are two different types of Statements of Performance Capabilities that may be verified in this testing. Examples include to statements shown in Table 3.1:

**Table 3.1: Example Statements of Performance Capabilities for SOC Removal**

<b>Type of Statement of Performance Capabilities</b>	<b>Example of Statement of Performance Capabilities</b>
<b>SOC Removal</b>	This packaged plant is capable of achieving 98 percent removal of the SOC chlordane 60-day operation period at a flux of 15 gpm/sf (75 percent recovery; temperature between 20 and 25 °C) in feedwaters with chlordane concentrations less than 0.1 µg/L and total dissolved solids concentrations less than 500 mg/L.
<b>Regulatory Compliance</b>	This packaged plant is capable of producing a product water meeting the National Primary Drinking Water Standards for chlordane concentration during a 60-day operation period at a flux of 15 gpm/sf (75 percent recovery; temperature between 20 and 25 °C) in feedwaters with chlordane concentrations less than 0.1 µg/L and total dissolved solids concentrations less than 500 mg/L.

An example of a Statement of Performance Capabilities that would not be acceptable is presented below:

"This packaged plant will achieve removal of SOC's in accordance with the Safe Drinking Water Act (SDWA) on a consistent and dependable basis."

The Statement of Performance Capabilities shall identify the water quality objectives to be achieved by the equipment and evaluated in the verification testing. For each Statement of Performance Capabilities proposed by the FTO and the Manufacturer in the FOD, the following information shall be provided:

- Applications of the equipment;
- Known limitations of the equipment;
- Advantages it provides over existing equipment;
- Percent removal of the targeted SOC;
- Rate of treated water production (i.e., flux);
- Product water recovery;

- Feed stream water quality regarding pertinent water quality parameters;
- Temperature;
- Concentration of targeted SOC; and
- Other pertinent water quality and operational conditions.

During Verification Testing, the FTO must demonstrate that the equipment is operating at a steady-state prior to collection of data to be used in verification of the Statement of Performance Capabilities. The following equation shall be used to determine percent removal of the SOC investigated:

$$\text{Percent SOC Removal} = \left[ 1 - \frac{\text{Finished Water SOC Concentration}}{\text{Feed Water SOC Concentration}} \right] * 100\%$$

The FTO on behalf of the Manufacturer shall be responsible for identification of which SOC shall be monitored and recorded for testing under the Statement of Performance Capabilities in the FOD. The analysis of SOC's in the feedwater, treated water and wastewater streams shall be performed by a state-certified, third-party accredited or EPA-accredited laboratory using an approved Standard Method.

The Statement of Performance Capabilities prepared by the FTO (in collaboration with the Manufacturer) shall also indicate the range of water quality under which the equipment can be challenged while successfully treating the feedwater. Statements of Performance Capabilities that are not too easily met may not be of interest to the potential user, while performance capabilities that are overstated may not be achievable. If a manufacturer relies on integrated physio-chemical processes for SOC removal, the Statement of Performance Capabilities must include the overall packaged and/or modular water treatment system SOC removal performance. The Statement of Performance Capabilities forms the basis of the entire Equipment Verification Testing Program and must be chosen appropriately. Therefore, the design of the FOD should include a sufficient range of feedwater quality to permit verification of the Statement of Performance Capabilities.

It should be noted that many of the packaged and/or modular drinking water treatment systems participating in the SOC Removal Verification Testing Program will be capable of achieving multiple water treatment objectives. Although this Protocol and the associated Verification Testing Plans are oriented towards removal of SOC's from feedwaters, the Manufacturer may want to look at the treatment system's removal capabilities for additional water quality parameters.

### **3.2 Equipment Description**

Description of the equipment for Verification Testing shall be included in the FOD. Data plates shall be permanent and securely attached to each production unit. The data plate shall be easy to read in English or the language of the intended user, located on the equipment where it is readily accessible, and contain at least the following information:

- Equipment Name

- Model Number
- Manufacturer's name and address
- Electrical requirements - volts, amps, hertz and phase
- Equipment size and weight
- Shipping requirements and special handling precautions
- Equipment maintenance requirements
- Serial Number
- Warning and Caution statements in legible and easily discernible print size
- Capacity or output rate (if applicable)

In addition, the Manufacturer must provide the equipment with all OSHA required safety devices (if applicable).

***Content of FOD Regarding Equipment Capabilities and Description:***

*The FOD shall include the following:*

- *Description of the equipment to be demonstrated including photographs from several perspectives.*
- *Brief introduction and discussion of the engineering and scientific concepts on which the SOC removal capabilities of the water treatment equipment are based.*
- *Description of the package treatment plant and each process included as a component in the modular system including all relevant schematics of treatment and pretreatment systems.*
- *Brief description of the physical construction/components of the equipment, including the general environment requirements and limitations, required consumables; weight, transportability, ruggedness, power and other pertinent information needed, etc.*
- *Statement of typical rates of consumption of chemicals, a description of the physical and chemical nature of wastes, and the rates of waste generation (concentrates, residues, waste products, required regeneration frequencies; materials replacement frequencies; etc.).*
- *Definition of the performance range of the equipment.*
- *Identification of any special licensing requirements associated with the operation of the equipment.*
- *Description of the applications of the equipment and the removal capabilities of the treatment system relative to existing equipment. Comparisons shall be provided in such areas as: treatment capabilities, requirements for chemicals and materials, power, labor requirements, suitability for process monitoring and operation from remote locations, ability to be managed by part-time operators.*

- *Discussion of the known limitations of the equipment. The following operational details shall be included: the range of feedwater quality suitable for treatment with the equipment, the upper limits for concentrations of regulated contaminants that can be removed to concentrations below the MCL, level of operator skill required to successfully use the equipment.*

## 4.0 EXPERIMENTAL DESIGN

This section discusses the objectives of the Verification Testing, factors that must be considered to meet the performance objectives, and the statistical analysis and other means that the FTO will use to evaluate the results of the Verification Testing.

### 4.1 Objectives

The objectives of this Verification Testing are to evaluate equipment in the following areas:

1. Performance relative to the Manufacturer's stated range of SOC removal capabilities and equipment operation.
2. Performance of SOC removal relative to SOC action levels and as applicable, any maximum contaminant levels (MCLs) stipulated by the National Primary Drinking Water Standards and the EPA National Secondary Drinking Water Regulations or other specific or anticipated water quality regulations (if desired by the Manufacturer and FTO).
3. The impacts of variations in feedwater quality (such as DOC, temperature, turbidity, microbial concentration, pH, alkalinity, etc.) on equipment performance.
4. The logistical, human, and economic resources necessary to operate the equipment.
5. The reliability, ruggedness, cost factors, range of usefulness, and ease of operation.
6. Identify the secondary impacts of treatment relative to other SDWA regulations (such as the Lead and Copper Rule).

The Manufacturer shall be responsible for selection of those treatment challenges listed in NSF test plans that are most appropriate for their equipment. For example, if equipment were only intended for removal of SOC, there would be no need to conduct testing to evaluate the removal of hardness ions or metal ion species. However, it should be noted that many of the packaged and/or modular drinking water treatment systems participating in the SOC Removal Verification Testing Program might be capable of achieving multiple water treatment objectives. The Verification Testing Program may for example be undertaken to demonstrate equipment removal capabilities for a wide number of constituents. In addition, the FTO and the Manufacturer may wish to construct the FOD so that Verification Testing may also demonstrate the treatment system's removal capabilities and treatment operations for additional water quality parameters. The incorporation of additional treatment objectives may also necessitate attention to the other applicable protocol and test plan documents in the development of the FOD.

## **4.2 Equipment Characteristics**

This section discusses equipment characteristics or factors that will be considered in the design and implementation of the Equipment Verification Testing Program. These factors include

- ease of operation;
- degree of operator attention required;
- response of equipment and treatment process to changes in feedwater quality;
- electrical requirements;
- system reliability features including redundancy of components;
- feed flow requirements;
- discharge requirements;
- spatial requirements of the equipment (footprint);
- unit processes included in treatment train;
- chemicals needed;
- chemical hazards associated with equipment operation; and
- response of treatment process to intermittent operation.

Verification Testing procedures shall simulate routine conditions as much as possible and in most cases testing may be done in the field. Under such circumstances, simulation of field conditions would not be necessary.

### **4.2.1 Qualitative Factors**

Some factors, while important, are difficult or impractical to quantify. These are considered qualitative factors. Important factors that cannot easily be quantified are the modular nature of the equipment, ease of operation, the safety of the equipment, the portability of equipment, and the logistical requirements necessary for using it.

Typical qualitative factors to be discussed are listed below, and others may be added. The FOD shall discuss those factors that are appropriate to the test equipment, such as but not limited to the following:

- Reliability or susceptibility to environmental conditions
- Equipment safety
- Effect of operator experience on results
- Effect of operator's technical knowledge on system performance and robustness of operation

#### **4.2.2 Quantitative Factors**

Many factors of the equipment characteristics can be quantified by various means in this Verification Testing Program. Some can be measured while others cannot be controlled. Typical quantitative factors to be discussed are listed below, and others may be added. The FOD shall discuss those factors that are appropriate to the test equipment, such as but not limited to the following:

- Power and consumable supply (such as chemical and materials) requirements
- Productivity and performance of equipment
- Monitoring requirements for pressure, flow, and temperature
- Cost of operation, expendables and waste disposal
- Hydrodynamics of packaged plant system
- Chemical equivalents of process streams
- Safety features of equipment
- Length of operating cycle
- Daily labor hours required for operation and maintenance

These quantitative factors will be used as an initial benchmark to assess equipment performance.

#### **4.3 Water Quality Considerations**

The primary treatment goal of the equipment employed in this Verification Testing Project through this protocol is to achieve removal of SOC<sub>s</sub> found in feedwaters (or raw waters) such that finished waters are of acceptable water quality. Depending upon the goals of the equipment Manufacturer, the driving force for Verification Testing of SOC removal under a specific set of operating and feedwater quality conditions. The objectives of Verification Testing may also be to achieve compliance with the National Primary Drinking Water Standards and the EPA National Secondary Drinking Water Regulations in many cases, and assure production of water with palatable, healthful and consistent water quality. The experimental design and Statement of Performance Capabilities in the FODs shall be developed so the relevant questions about water treatment equipment capabilities can be answered.

Manufacturers should carefully consider the capabilities and limitations of their equipment and have their Statement of Performance Capabilities sufficiently challenge their equipment. The FTO on behalf of the Manufacturer should adopt an experimental approach to verification testing that would provide a broad market for their products, while recognizing the limitations of the equipment. The FTO should not adopt a verification experimental approach to removal of SOC<sub>s</sub> that would be beyond the capabilities of the equipment. A wide range of contaminants or water quality problems that can be addressed by water treatment equipment varies, and some packaged treatment equipment can address a broader range of problems than other types. Manufacturers shall use NSF Equipment Verification Testing Plans as the basis for the development of the experimental plan in each specific FOD.



#### **4.3.1 Feed Water Quality**

One of the key aspects related to demonstration of equipment performance in the Verification Testing Project is the range of feedwater quality that can be treated successfully. The Manufacturer and FTO should consider the influence of feedwater quality on the quality of treated waters produced by the packaged plant, such that product waters meet the designated water quality goals stated in the FOD and were applicable, as driven by water quality goals, National Primary Drinking Water Standards and the EPA National Secondary Drinking Water Regulations. As the range of feed water quality that can be treated by the equipment becomes broader, the potential applications for treatment equipment with verified performance capabilities might also increase.

The FTO shall provide a list of SOC's in the FOD that may be pertinent in equipment performance for removal of SOC's. Characteristics of feedwater quality that may be important for treatment equipment intended to remove SOC's should be identified in the applicable FOD.

One of the questions often asked by regulatory officials in approval of packaged water treatment equipment is: "Has it been shown to work on the water where it is proposed to be used?" By covering a large range of water qualities the Verification Testing is more likely to provide an affirmative answer to that question.

#### **4.3.2 Treated Water Quality**

Production of treated water of a high quality, having no trace of SOC shall be the primary goal of the packaged and/or modular water treatment systems included in this Equipment Verification Testing Project. If a FTO states that water treatment equipment can be used to treat water to meet specified regulatory requirements for removal of SOC's, the Verification Testing must provide data that support such a Statement of Capabilities, as appropriate. Where desired by the Manufacturer, the Statement of Performance Capabilities provided by the FTO shall be related to percent removal capabilities or to the National Primary Drinking Water Standards and the EPA National Secondary Drinking Water Regulations.

The FTO on behalf of the Manufacturer shall be responsible for identification of the specific SOC's that shall be monitored during the Equipment Verification Testing Program. A state-certified, third-party accredited or EPA accredited laboratory shall perform water quality analysis for the specific SOC's identified in water samples provided by the FTO. This issue shall be discussed further in Section 5.2.

In addition, the FTO may wish to make a statement about performance capabilities of the equipment for removal of other unregulated, or regulated contaminants under the National Primary and Secondary Drinking Water Standards that are not directly related to SOC removal. For example, some water treatment equipment can be used to meet aesthetic goals that are not included as National Drinking Water requirements of the SDWA. Removal goals for some of these parameters may also be presented in the FOD as additional Statements of Performance Capabilities.

#### **4.4 Synthetic Organic Chemical Contaminants Testing**

Because of the numerous varieties of SOC, analytical procedures must be approved or proven techniques. Many methods for SOC analysis are outlined in Standard or EPA Methods and shall be employed in this Verification Testing Program evaluation of SOC. Should an approved method be non-existent for an individual SOC, then a proposed method may be allowed after at least 3 labs have successfully demonstrated the method to achieve a standard degree of uncertainty in analysis. The manufacturer would be required to document and submit details of analytical procedures used to measure the specific SOC.

Frequency of sampling and SOC analysis shall be specified by the individual test plans used for the Equipment Verification Testing Program and shall also be stipulated in the FOD.

#### **4.5 Recording Data**

For all SOC experiments targeted towards removal of SOC, water quality data on feedwater, finished water, and wastewater should be maintained at a minimum on the identified SOC and other water quality parameters identified by the FTO. The specific water quality parameters to be monitored and with what frequency shall be stipulated in the test plan employed for development of the FOD prior to initiation of the Verification Testing Program. At a minimum, the following conditions shall also be maintained for each experiment:

- Water type (raw water, pretreated feed water, product water, waste water);
- Experimental run (e.g. 1<sup>st</sup> run, 2<sup>nd</sup> run, 3<sup>rd</sup> run, etc.);
- Type of chemical addition, dose and chemical combination, where applicable (e.g., alum, cationic polymer, anionic polymer, ozone, monochloramine, scale inhibitor, etc.);
- Rate of flow through system, volume waste production as percent finished water flow, cumulative flow through system in terms of bed volumes (where applicable);
- Transmembrane pressure, membrane flux and element recovery (for membrane processes where applicable);
- Chemical cleaning frequency or regeneration frequency (where applicable);
- Voltage requirements, current draw and power consumption at specific operating conditions.

#### **4.6 Recording Statistical Uncertainty**

For the analytical data obtained during verification testing, 95 percent confidence intervals shall be calculated by the FTO for selected water quality parameters. The FTO shall ensure in the FOD that sufficient water quality data and operational data are collected to allow estimation of statistical uncertainty. The specific testing plans that may be employed with the Protocol stipulate only a minimum frequency for monitoring of SOC. The FTO shall therefore ensure that sufficient water quality and operational data is collected during Verification Testing for the statistical analysis described herein. The specific testing plans shall specify which water quality parameters shall be subjected to the requirements of confidence interval calculation. The specific

testing plans shall specify which water quality parameters shall be subjected to the requirements of confidence interval calculation. As the name implies, a confidence interval describes a population range in which any individual population measurement may exist with a specified percent confidence. The following formula shall be employed for confidence interval calculation:

$$\text{Confidence Interval} = \bar{x} \pm t_{n-1, 1-\frac{\alpha}{2}} \left( \frac{S}{\sqrt{n}} \right)$$

where:  $\bar{x}$  = sample mean

S = sample standard deviation

n = number of independent measurements included in the data set

t = Student's t distribution value with n-1 degrees of freedom

$\alpha$  = significance level, defined for 95 percent confidence as:  $1 - 0.95 = 0.05$

According to the 95 percent confidence interval approach, the  $\alpha$  term is defined to have the value of 0.05, thus simplifying the equation for the 95 percent confidence interval in the following manner:

$$95\% \text{ Confidence Interval} = \bar{x} \pm t_{n-1, 0.975} \left( \frac{S}{\sqrt{n}} \right)$$

With input of the analytical results for pertinent water quality parameters into the 95 percent confidence interval equation, the output will appear as the sample mean value plus or minus the confidence term. The results of this statistical calculation may also be presented as a range of values falling within the 95 percent confidence interval. For example, the results of the confidence interval calculation may provide the following information:  $520 \pm 38.4$  mg/L, with a 95 percent confidence interval range described as (482, 558).

Calculation of confidence intervals shall not be required for equipment performance results (e.g., filter run length, cleaning efficiency, in-line turbidity or in-line particle counts, etc.) obtained during the equipment Testing Verification Program. However, as specified by the FTO, calculation of confidence intervals may be required for analytical parameters such as SOC and NPDOC. In order to provide sufficient analytical data for statistical analysis, the FTO shall collect three discrete water samples at one set of operational conditions for each of the specified water quality parameters during a designated testing period. The procedures and sampling requirements shall be provided in detail in the Verification Testing Plan.

#### **4.7 Verification Testing Schedule**

Verification testing activities include equipment set-up, initial operation, verification operation, and sampling and analysis. Initial operations are intended to be conducted so that equipment can be tested to be sure it is functioning as intended. If feed water (or source water) quality influences operation and performance of equipment being tested, the initial operations period serves as the "shake-down" period for determining appropriate operating parameters. The schedule of testing may also be influenced by coordination requirements with a utility.

For water treatment equipment involving removal of SOC<sub>s</sub>, an initial period of bench-scale testing of feedwater followed by treatment equipment operation may be needed to determine the appropriate operational parameters for testing equipment. A number of operational parameters may require adjustment to achieve successful functioning of the process train. These parameters may include but are not limited to the following: process rates; feed water pH; chemical dosages, chemical types (where appropriate) and other parameters that may result in successful functioning of the process train. Chemical type, chemical dosages, and other operations that result in successful functioning of the packaged process should be included.

It is recommended under this protocol that a minimum of one 60-day test period of Verification Testing be conducted in order to allow testing over a period of time to collect representative data. The specific operating and water quality parameters shall be stipulated by the selected Test Plan under this protocol and shall be used in development of the experimental plan and the preparation of the FOD.

### ***Content of FOD Regarding Experimental Design***

*The FOD shall include the following elements:*

- *Identification of the qualitative and quantitative factors of equipment operation to be addressed in the Verification Testing Program.*
- *Identification and discussion of the particular water treatment issues and SOC concentrations that the equipment is designed to address, how the equipment will solve the problem, and who would be the potential users of the equipment.*
- *Identification of the range of key water quality parameters, given in applicable NSF Testing Plans, which the equipment is intended to address and for which the equipment is applicable.*
- *Identification of the key parameters of treated water quality and analytical methods that will be used for evaluation of equipment performance during the removal of SOC<sub>s</sub>. Parameters of significance for treated water quality are listed in applicable NSF Testing Plans.*
- *Description of data recording protocol for equipment operation, feed water quality parameters, and treated water quality parameters.*
- *Description of the confidence interval calculation procedure for selected water quality parameters.*
- *Detailed outline of the Verification Testing schedule, with regard to annual testing periods that will cover an appropriate range of annual climatic conditions, (i.e., different temperature conditions, seasonal differences between rainy and dry conditions).*

## **5.0 FIELD OPERATIONS PROCEDURES**

### **5.1 Equipment Operations and Design**

The NSF Verification Testing Plan specifies procedures that shall be used to provide accurate documentation of both equipment performance and treated water quality. Careful adherence to these procedures will result in definition of verifiable performance of equipment. The specific reporting techniques, methods of statistical analysis and the QA/QC of reporting SOC removal data shall be stated explicitly by the FTO in the FOD before initiation of the Verification Testing Program. (Note that this protocol may be associated with a number of different NSF Equipment Verification Testing Plans for different types of process equipment capable of achieving removal of SOCs).

The design aspects of water treatment process equipment often provide a basis for approval by State regulatory officials and can be employed under higher or lower flow rate conditions. The field operations procedures and testing conditions provided by the FTO shall therefore be specified to demonstrate treatment capabilities over a broad range of operational conditions and feedwater qualities.

Initial operations of the SOC removal equipment will allow FTOs to refine the equipment operating procedures and to make operational adjustments as needed to successfully treat the feedwater. Information generated through this period of operation may be used to revise the FOD, if necessary. A failure at this point in the Verification Testing could indicate a lack of capability of the process equipment and the Verification Testing might be cancelled. Specific design aspects to be included in the FOD are provided in detail, in the Manufacturer Responsibilities section below.

### **5.2 Selection of Analytical Laboratory and Field Testing Organization**

To assess the performance of the equipment, the quality of the treated water produced using the equipment shall be determined by analysis at a State-certified, third-party accredited or EPA-accredited analytical laboratory with proven experience in detection and measurement of SOCs. In all cases, current EPA Standard Methods procedures shall be used in analysis of specified water quality parameters. Because of the variability of acceptance of laboratories from state to state, use of analytical laboratories certified in a large number of states is recommended. Furthermore, the selected analytical laboratory must be certified by the state in which the Verification Testing is being performed. Analytical results from the laboratory are to be provided directly to the NSF to maintain data integrity.

For field testing operations, the Manufacturer shall employ an NSF-qualified FTO; the list of qualified organizations may include engineering consulting firms, universities, or other qualified scientific organizations with experience operating pilot plant equipment. If a particular SOC does not have an accepted standard method procedure, then an analytical testing plan shall be submitted to NSF describing the procedure.

### **5.3 Communications, Documentation, Logistics, and Equipment**

NSF shall communicate regularly with the Verification Testing participants to coordinate all field activities associated with this Verification Testing and to resolve any logistical, technical, or QA/QC issues that may arise as the Verification Testing progresses. The successful implementation of the Verification Testing will require detailed coordination and constant communication between all Verification Testing participants.

All field activities shall be thoroughly documented. Field documentation will include:

- field logbooks;
- photographs;
- field data sheets; and
- chain-of-custody forms.

The qualified FTO shall be responsible for maintaining all field documentation. The field logbook shall have at least the following requirements.

- Field notes shall be kept in a bound logbook.
- Each page shall be sequentially numbered and labeled with the project name and number.
- Field logbooks shall be used to record all water treatment equipment operating data.
- Completed pages shall be signed and dated by the individual responsible for the entries.
- Errors shall have one line drawn through them and this line shall be initialed and dated.

All photographs shall be logged in the field logbook. These entries shall include the time, date, direction, subject of the photograph, and the identity of the photographer. Deviations from the approved final FOD shall be thoroughly documented in the field logbook at the time of inspection and in the verification report.

Original field sheets and chain-of-custody forms shall accompany all samples shipped to the analytical laboratory. Copies of field sheets and chain-of-custody forms for all samples shall be provided at the time of the QA/QC inspection and included in the verification report.

As available, electronic data storage and retrieval capabilities shall be employed in order to maximize data collection and minimize labor hours required for monitoring. The guidelines for use of data-loggers, laptop computers, data acquisition systems etc., shall be detailed by the FTO in the FOD.

### **5.4 Initial Operations**

Initial operations of the SOC removal equipment will allow the FTO to refine their operating procedures and to make operational adjustments as needed to successfully treat the feedwater. Information generated through this period of operation may be used to revise the FOD, if

necessary. A failure at this point in the Verification Testing could indicate a lack of capability of the process equipment and the Verification Testing might be canceled.

## **5.5 Equipment Operation and Water Quality Sampling for Verification Testing**

All field activities shall conform to requirements provided in the FOD that was developed and NSF-approved for the Verification Testing being conducted. All sampling and sample analysis conducted during the Verification Testing Program shall be performed according to the procedures detailed by the FTO in the FOD. As necessary for Verification analysis, state-certified or third-party or EPA-qualified laboratories are selected to perform analytical services using approved Standard or EPA Methods.

If unanticipated or unusual situations are encountered that may alter the plans for equipment operation, water quality sampling, or data quality, the situation must be discussed with the NSF technical lead. Any deviations from the approved final FOD shall be thoroughly documented.

During routine operation of water treatment equipment, the total number of hours during which the equipment is operated each day shall be documented. In addition, the number of hours each day during which the operator was working at the treatment plant performing tasks related to water treatment and the operation of the treatment equipment shall be documented. Furthermore, the qualified Testing Organization, the Water System or the Plant Operator shall describe the tasks performed during equipment operation.

### ***Content of FOD Regarding Field Operations Procedures***

*The FOD shall include the following elements:*

- *A table summary of the proposed time schedule for operating and testing.*
- *Field operating procedures for the equipment and performance testing, based upon the NSF Equipment Verification Testing Plan with listing of operating parameters, ranges for feedwater quality, and sampling and analysis strategy.*
- *Provision of all equipment needed for fieldwork associated with this Verification Testing.*
- *Provision of a complete list of all equipment to be used in the Verification Testing. A table format is suggested.*
- *Provision of field operating procedures.*

## **6.0 QUALITY ASSURANCE PROJECT PLAN**

The quality assurance project plan (QAPP) for this Verification Testing specifies procedures that shall be used to ensure data quality and integrity. Careful adherence to these procedures will ensure that data generated from the Verification Testing will provide sound analytical results that can serve as the basis for performance verification.



## **6.1 Purpose and Scope**

The purpose of this section is to outline steps that shall be taken by operators of the equipment and by the analytical laboratory to ensure that data resulting from this Verification Testing is of known quality and that a sufficient number of critical measurements are taken.

## **6.2 Quality Assurance Responsibilities**

The FTO project manager is responsible for coordinating the preparation of the QAPP for this Verification Testing and for its approval by the NSF. The qualified testing organization project manager, with oversight from NSF, shall also ensure that the QAPP is implemented during all Verification Testing activities.

The Manufacturer and the NSF must approve the entire FOD including the QAPP before the Verification Testing can proceed. The NSF must review and either approve the QAPP or provide reasons for rejection of the QAPP. They should also provide suggestions on how to modify the QAPP to make it acceptable, provided that the Manufacturer has made a good faith effort to develop an acceptable QAPP (i.e. the QAPP is 75 to 80 percent acceptable with only minor changes needed to produce an acceptable plan. NSF will not write QAPPs for Manufacturers.).

A number of individuals may be responsible for monitoring equipment operating parameters and for sampling and analysis QA/QC throughout the Verification Testing. Primary responsibility for ensuring that both equipment operation and sampling and analysis activities comply with the QA/QC requirements of the FOD shall rest with the FTO. QA/QC activities for the equipment shall include those activities recommended by the Manufacturer and those required by the NSF to assure the Verification Testing will provide data of the necessary quality.

QA/QC activities for the state-certified or third-party or EPA-qualified analytical laboratory that analyzes samples sent off-site shall be the responsibility of that analytical laboratory's supervisor. If problems arise or any data appear unusual, they shall be thoroughly documented and corrective actions shall be implemented as specified in this section. The QA/QC measurements made by the off-site analytical laboratory are dependent on the analytical methods being used.

## **6.3 Data Quality Indicators**

The data obtained during the Verification Testing must be of sound quality for conclusions to be drawn on the equipment. For all measurement and monitoring activities conducted for equipment verification, the NSF and EPA require that data quality parameters be established based on the proposed end uses of the data. Data quality parameters include four indicators of data quality:

- Accuracy;
- Precision;
- Representativeness; and
- Statistical Uncertainty



Treatment results generated by the equipment and by the laboratory analyses must be verifiable for the purposes of this program to be fulfilled. High quality, well-documented analytical laboratory results are essential for meeting the purpose and objectives of this Verification Testing. Therefore, the following indicators of data quality shall be closely evaluated to determine the performance of the equipment when measured against data generated by the analytical laboratory.

### 6.3.1 Accuracy

For water quality analyses, accuracy refers to the difference between a sample result and the reference or true value for the sample. Loss of accuracy can be caused by such processes as:

- Errors in standards preparation;
- Equipment calibrations;
- Loss of target analyte in the extraction process;
- Interferences; and
- Systematic or carryover contamination from one sample to the next.

In this Verification Testing, accuracy will be ensured by

- Maintaining consistent sample collection procedures, including sample locations;
- Timing of sample collection;
- Sampling procedures;
- Sample preservation;
- Sample packaging;
- Sample shipping; and
- Random spiking procedures for the specific inorganic constituents chosen for testing.

The FTO shall discuss the applicable ways of determining the accuracy of the chemical and microbiological sampling and analytical techniques in the FOD.

For water quality analysis, accuracy is usually expressed as the percent recovery. Percent recovery is the amount recovered during analysis. In general percent recovery can be calculated by dividing the measured amount added by the amount actually added.

$$\text{Percent Recovery} = \left( \frac{\text{Measured}_{\text{Sample + Spike}} - \text{Measured}_{\text{Sample}}}{\text{Actual}_{\text{Spike}}} \right) 100\% = \left( \frac{\text{Measured}_{\text{Spike}}}{\text{Actual}_{\text{Spike}}} \right) 100\%$$

For equipment operating parameters, accuracy refers to the difference between the reported operating condition and the actual operating condition. For equipment operating

data, accuracy entails collecting a sufficient quantity of data during operation to be able to detect a change in operations. For water flow, accuracy may be the difference between the reported flow indicated by a flow meter and the flow as actually measured on the basis of known volumes of water and carefully defined times (bucket and stopwatch technique) as practiced in hydraulics laboratories or water meter calibration shops. For mixing equipment, accuracy is the difference between an electronic readout for equipment rotations per minute (rpms) and the actual measurement based on counted revolutions and measured time. Accuracy of head loss measurement can be determined by using measuring tapes to check the calibration of piezometers for gravity filters or by checking the calibration of pressure gauges for pressure filters. Meters and gauges must be checked periodically for accuracy, and when proven to be dependable over time, the time interval between accuracy checks can be increased. In the FOD, the FTO shall discuss the applicable ways of determining the accuracy of the operational conditions and procedures.

### 6.3.2 Precision

Precision refers to the degree of mutual agreement among individual measurements and provides an estimate of random error. The standard deviation and the relative percent deviation recorded from sample analyses may be reported as a means to quantify sample precision. Precision measures the repeatability of measurement. It is usually expressed as the percent relative standard deviation (percent RSD). In general percent RSD can be calculated by dividing the standard deviation by the average. The methods to be employed for use of deviation shall be described by the FTO in the FOD.

$$\text{Percent RSD} = \left( \frac{\text{Standard Deviation}}{\text{Average}} \right) 100\% = \left( \frac{\sqrt{\frac{\sum_{i=1}^n (y_i - \bar{y})^2}{n-1}}}{\frac{\sum_{i=1}^n y_i}{n}} \right) 100\%$$

$y_i$  = sample measurement

$n$  = number of samples

### 6.3.3 Representativeness

Representativeness refers to the degree to which the data accurately and precisely represent the conditions or characteristics of the parameter represented by the data. In this Verification Testing, representativeness will be ensured by maintaining consistent sample collection procedures, including:

- Sample locations;
- Timing of sample collection;
- Sampling procedures;

- Sample preservation;
- Sample packaging;
- Sample shipping;
- Sample equipment decontamination; and
- Blind spikes.

Using each method at its optimum capability to provide results that represent the most accurate and precise measurement that it is capable of achieving also will ensure representativeness. For equipment operating data, representativeness entails collecting a sufficient quantity of data during operation to be able to detect a change in operations.

#### **6.3.4 Statistical Uncertainty**

Statistical uncertainty of the water quality parameters analyzed shall be evaluated through calculation of the 95 percent confidence interval around the sample mean. Description of the confidence interval calculation is provided in Section 4.6 – Recording Statistical Uncertainty.

### **6.4 Water Quality and Operational Control Checks**

This section describes the QC requirements that apply to both the treatment equipment and the on-site measurement of water quality parameters. It also contains a discussion of the corrective action to be taken if the QC parameters fall outside of the evaluation criteria.

The quality control checks provide a means of measuring the quality of data produced. The FTO may not need to use all of the checks identified in this section. The selection of the appropriate quality control checks depends on the following:

- Equipment
- Experimental design
- Performance goals

The selection of quality control checks will be based on discussions among the FTO and NSF. Some types of quality control checks applicable to operating water treatment equipment were described in Section 6.3.3.

#### **6.4.1 Quality Control for Equipment Operation**

This section will explain the methods to be used to check on the accuracy of equipment operating parameters and the frequency with which these quality control checks will be made. A key aspect of the Equipment Verification Testing Program is to provide operating results that will be widely accepted by State regulatory officials. If the quality of the equipment operating data can not be verified, then the water quality analytical results may be of no value. Because water can not be treated if equipment is not operating within specification, obtaining valid equipment operating data is a prime concern for Verification Testing.

An example of the need for QC for equipment operations is an incident of rejection of test data because the treatment equipment had no flow meter to use for determining engineering and operating parameters related to flow.

## **6.4.2 Water Quality Data**

After treatment equipment is operating within specifications and water is being treated, the results of the treatment are interpreted in terms of water quality. Therefore the quality of water sample analytical results is just as important as the quality of the equipment operating data. Therefore, the QAPP must emphasize the methods to be employed for sampling and analytical QA. The important aspects of sampling and analytical QA are given below:

**6.4.2.1 Duplicate Analysis of Selected Water Quality Parameters.** Duplicate samples shall be analyzed for selected water quality parameters at specified intervals in order to determine the precision of analysis. The procedure for determining samples to be analyzed in duplicate shall be provided in each Verification Testing Plan with the required frequency of analysis and the approximate number. The duplicate analysis shall be performed according to the requirements for calculation of 95 percent confidence intervals, as presented in Section 4.6.

**6.4.2.2 Method Blanks.** Method blanks are used for selected water quality parameters to evaluate analytical method-induced contamination, which may cause false positive results.

**6.4.2.3 Spiked Samples.** The use of spiked samples will depend on the testing program, and the contaminants to be removed. If spiked samples are to be used, specify the procedure, frequency, acceptance criteria, and actions if criteria are not met.

**6.4.2.4 Travel Blanks.** Travel blanks for selected water quality parameters shall be provided to the analytical laboratory to evaluate travel-related contamination.

**6.4.2.5 Performance Evaluation Samples for On-Site Water Quality Testing.** Performance evaluation (PE) samples are samples whose composition is unknown to the analyst. These are also known as blind spikes. Analysis of PE samples shall be conducted for selected water quality parameters before pilot testing is initiated by submission of samples to the analytical laboratory and to the equipment testing organizations, if appropriate. Control limits for the PE samples will be used to evaluate the equipment testing organization's and analytical laboratory's method performance. One kind of PE sample that would be used for on-site QA in most studies done under this protocol would be a turbidity PE sample.

PE samples come with statistics about each sample, which have been derived from the analysis of the sample by a number of laboratories using EPA-approved methods. These statistics include the following:

- true value of the PE sample;
- mean of the laboratory results obtained from the analysis of the PE sample; and

- acceptance range for sample values.

The analytical laboratory is expected to provide results from the analysis of the PE samples that meet the performance objectives of the Verification Testing.

## **6.5 Data Reduction, Validation, and Reporting**

To maintain good data quality, specific procedures shall be followed during data

- Reduction;
- Validation; and
- Reporting.

These procedures are detailed below.

### **6.5.1 Data Reduction**

Data reduction refers to the process of converting the raw results from the equipment into concentration or other data in a form to be used in the comparison. The procedures to be used will be equipment dependent. The purpose of this step is to provide data, which will be used to verify the Statement of Performance Capabilities. These data shall be obtained from logbooks, instrument outputs, and computer outputs as appropriate.

### **6.5.2 Data Validation**

The operator shall verify the completeness of the appropriate data forms and the completeness and correctness of data acquisition and reduction. The field team supervisor or another technical person shall review calculations and inspect laboratory logbooks and data sheets to verify precision, accuracy and completeness. The individual operators and the laboratory supervisor will examine calibration and QC data. Laboratory and project managers shall verify that all instrument systems are in control and those QA objectives for precision, accuracy, completeness, and method detection limits have been met.

Analytical outlier data are defined as those QC data lying outside a specific QC objective window for precision and accuracy for a given analytical method. Should QC data be outside of control limits, the analytical laboratory or field team supervisor will investigate the cause of the problem. If the problem involves an analytical problem, the sample will be reanalyzed. If the problem can be attributed to the sample matrix, the result will be flagged with a data qualifier. This data qualifier will be included and explained in the final analytical report.

### **6.5.3 Data Reporting**

The data reported during the Verification Testing Program shall be explicitly defined by the FTO in the FOD. At a minimum, the data tabulation shall list the results for feedwater and treated water quality analyses, the results of SOC removal analyses and equipment operating data. All QC information such as calibrations, blanks and reference

samples are to be included in an appendix. All raw analytical data shall also be reported in an appendix. All data shall be reported in hardcopy and electronically in a common spreadsheet or database format.

## **6.6 System Inspections**

On-site system inspections for sampling activities, field operations, and laboratories shall be conducted as specified by the NSF Equipment Verification Testing Plan. These inspections will be performed by the verification entity to determine if the NSF Equipment Verification Testing Plan is being implemented as intended. At a minimum, NSF shall conduct one audit of the sampling activities, field operations program and laboratories during the Verification Testing. The number of audits performed during a study shall be specified by the pertinent Equipment Verification Testing Plan. Separate inspection reports will be completed after the audits and provided to the participating parties.

## **6.7 Reports**

### **6.7.1 Status Reports**

The FTO shall prepare periodic reports for distribution to pertinent parties, e.g., manufacturer, EPA, the community. These reports shall discuss:

- project progress;
- problems and associated corrective actions; and
- future scheduled activities associated with the Verification Testing.

Each report shall include an executive summary at the beginning of the report to introduce the salient issues of the testing period. When problems occur, the Manufacturer and FTO project managers shall discuss them, and estimate the type and degree of impact, and describe the corrective actions taken to mitigate the impact and to prevent a recurrence of the problems. The frequency, format, and content of these reports shall be outlined in the FOD.

### **6.7.2 Inspection Reports**

Any QA inspections that take place in the field or at the analytical laboratory while the Verification Testing is being conducted shall be formally reported by the

- FTO;
- Verification entity; and
- Manufacturer.

## **6.8 Corrective Action**

Each FOD must incorporate a corrective action plan. This plan must include the predetermined acceptance limits, the corrective action to be initiated whenever such acceptance criteria are not met, and the names of the individuals responsible for implementation.

Routine corrective action may result from common monitoring activities, such as:

- Performance evaluation audits
- Technical systems audits

### ***Content of FOD Regarding Quality Assurance Project Plan***

*The FOD shall include the following elements:*

- *Description of methodology for measurement of accuracy.*
- *Description of methodology for measurement of precision.*
- *Description of the methodology for use of blanks, the materials used, the frequency, the criteria for acceptable method blanks and the actions if criteria are not met.*
- *Description of any specific procedures appropriate to the analysis of the PE samples.*
- *Outline of the procedure for determining samples to be analyzed in triplicate, the frequency and approximate number.*
- *Description of the procedures used to assure that the data are correct.*
- *Listing of techniques and/or equations used to quantify any necessary data quality indicator calculations in the analysis of water quality parameters. These include accuracy, precision, completeness (e.g., relative percent deviation, standard deviation, and confidence interval calculation).*
- *Outline of the frequency, format, and content of reports in the FOD.*
- *Development of a corrective action plan in the FOD.*

*The FTO shall be responsible for proving and including the following elements in the FOD:*

- *Provision of all QC information such as calibrations, blanks and reference samples in an appendix. All raw analytical data shall also be reported in an appendix.*
- *Provision of the inspection results in an appendix.*
- *Provision of all data in hardcopy and electronic form in a common spreadsheet or database format.*

## **7.0 DATA MANAGEMENT, ANALYSIS AND REPORTING**

### **7.1 Data Management and Analysis**

The responsibilities of the FTO for data management and analysis have been provided in the Responsibilities Summary Sheet, the Project Guidance Manual, and/or the Terms and Conditions cited earlier in this protocol. The Manufacturer, qualified FTO and NSF each have distinct responsibilities for managing and analyzing Verification Testing data. The equipment FTO is responsible for managing all the data and information generated during the Verification Testing. The Manufacturer is responsible for furnishing those records generated by the equipment FTO. NSF will be responsible for analysis and verification of the data.

A variety of data will be generated during a Verification Testing. Each piece of data or information identified for collection in the NSF Equipment Verification Testing Plan will need to be provided in the report. The data management section of the FOD shall describe what types of data and information needs to be collected and managed, and shall also describe how the data will be reported to the NSF for evaluation.

The raw data and the validated data must be reported. These data shall be provided in hard copy and in electronic format. As with the data generated by the innovative equipment, the electronic copy of the laboratory data shall be provided in a spreadsheet and a data dictionary shall be provided. In addition to the sample results, all QA/QC summary forms must be provided.

Other items that must be provided include:

- field notebooks
- photographs, slides and videotapes (copies)
- results from the use of other field analytical methods

## **7.2 Report of Equipment Testing**

The FTO shall prepare a draft report describing the Verification Testing that was carried out and the results of that testing. This report shall include the following topics:

- Introduction
- Executive Summary
- Description and Identification of Product Tested
- Procedures and Methods Used in Testing
- Results and Discussion
- Conclusions and Recommendations
- References
- Appendices
- Manufacturer FOD
- QA/QC Results
- Audit Report

The NSF will review the draft report, the results of testing, the audit report, the QA/QC results, and will issue a final report.

### ***Content of FOD Regarding Data Management and Analysis, and Reporting***

*The FOD shall include the following:*

- *Description of what types of data and information needs to be collected and managed.*



- *Description of how the data will be reported to the NSF for evaluation.*

## **8.0 SAFETY AND MAINTENANCE CONSIDERATIONS**

The safety procedures shall address safety considerations and include adherence to all local, State and Federal regulations relative to safety and operational hazards. The safety procedures shall address safety considerations, which relate to the health and safety of personnel require to work on the site of the test equipment and persons visiting the site. Many of these items will be covered by site inspections and construction and operating permits issued by responsible agencies. The safety procedures shall address safety considerations, including the following as applicable:

- Regulations covering the transport, storage, handling and disposal of hazardous chemicals including acids, caustic and oxidizing agents
- Chemical hazards and biohazards
- Conformance with the National Electric Code
- Provision of and access to fire extinguishers
- Provision of sanitary facilities
- Regulations covering site security
- Conformance to any building permit requirements, such as provision of handicap access or other health and safety requirements
- Ventilation of equipment or of trailers or buildings housing equipment, if gases generated by the equipment could present a safety hazard.

For additional information on pilot plant and laboratory safety see:

- i. Palluzi, R. P. Pilot Plant and Laboratory Safety. New York: McGraw-Hill, 1994
- ii. Fuscaldo, A. A., et al. Laboratory Safety, Theory and Practice. New York: Academic Press. 1980.

### ***Content of FOD Regarding Safety***

*The Manufacturer shall be responsible for:*

- *Provisions of required written material (such as Material Data Safety Sheets).*
- *Compliance with all safety requirements of local, State and Federal laws and regulators.*
- *Provisions of maintenance information and troubleshooting guidelines and instructions relative to the equipment to be verified.*

*The FOD shall include the following:*

- Address safety considerations that are appropriate for the equipment being tested and for the chemicals employed in the Verification Testing.

**CHAPTER 2**

**EPA/NSF ETV**

**EQUIPMENT VERIFICATION TESTING PLAN**

**FOR THE REMOVAL OF SYNTHETIC ORGANIC CHEMICAL CONTAMINANTS**

**BY MEMBRANE FILTRATION PROCESSES**

Prepared by:  
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## TABLE OF CONTENTS

	<u>Page</u>
<b>1.0 APPLICATION OF THIS NSF EQUIPMENT VERIFICATION TESTING PLAN</b> .....	2-6
<b>2.0 INTRODUCTION</b> .....	2-6
<b>3.0 GENERAL APPROACH</b> .....	2-7
<b>4.0 BACKGROUND</b> .....	2-8
4.1 Regulatory and Health Effects .....	2-8
4.2 SOC Removal by Membrane Processes .....	2-9
4.3 Membrane System Design Considerations .....	2-12
4.3.1 Pretreatment .....	2-12
4.3.1.1 Scaling .....	2-12
4.3.1.2 Colloidal Fouling .....	2-13
4.3.1.3 Microbiological Fouling .....	2-13
4.3.1.4 Chemical Fouling .....	2-13
4.3.2 Advanced Pretreatment .....	2-13
4.3.3 Membrane Processes .....	2-13
4.3.4 Post-Treatment .....	2-14
4.3.5 Waste Disposal .....	2-14
<b>5.0 DEFINITION OF OPERATIONAL PARAMETERS</b> .....	2-15
<b>6.0 OVERVIEW OF TASKS</b> .....	2-25
<b>7.0 TESTING PERIODS</b> .....	2-26
<b>8.0 TASK 1: CHARACTERIZATION OF RAW WATER</b> .....	2-27
8.1 Introduction .....	2-27
8.2 Objectives .....	2-27
8.3 Work Plan .....	2-27
8.4 Schedule .....	2-28
8.5 Evaluation Criteria .....	2-28
<b>9.0 TASK 2: MEMBRANE PRODUCTIVITY</b> .....	2-28
9.1 Introduction .....	2-28
9.2 Experimental Objectives .....	2-29
9.3 Work Plan .....	2-29
9.3.1 Operational Data Collection .....	2-30
9.3.2 Feedwater Quality Limitations .....	2-30

## TABLE OF CONTENTS (continued)

	<u>Page</u>
<b>10.0 TASK 3: FINISHED WATER QUALITY</b> .....	2-36
10.1 Introduction .....	2-36
10.2 Objectives.....	2-36
10.3 Work Plan.....	2-36
10.4 Analytical Schedule.....	2-39
10.4.1 Removal of SOCs.....	2-39
10.4.2 Feed and Permeate Water Characterization .....	2-39
10.4.3 Water Quality Sample Collection.....	2-39
10.4.4 Raw Water Quality Limitations .....	2-40
10.5 Evaluation Criteria and Minimum Reporting Requirements .....	2-40
<b>11.0 TASK 4: CLEANING EFFICIENCY</b> .....	2-40
11.1 Introduction .....	2-40
11.2 Experimental Objectives .....	2-41
11.3 Work Plan.....	2-41
11.4 Recommended Disposal Procedures .....	2-41
11.5 Analytical Schedule.....	2-42
11.5.1 Sampling.....	2-42
11.5.2 Operational Data Collection.....	2-42
<b>12.0 TASK 5: OPERATIONS AND MAINTENANCE MANUAL</b> .....	2-42
12.1 Objectives.....	2-42
12.2 O&M Work Plan .....	2-42
<b>13.0 TASK 6: DATA COLLECTION AND MANAGEMENT</b> .....	2-48
13.1 Introduction .....	2-48
13.2 Objectives.....	2-48
13.3 Work Plan.....	2-48
13.3.1 Data Handling Work Plan .....	2-48
13.3.2 Data Management.....	2-48
13.3.3 Statistical Analysis .....	2-49
<b>14.0 TASK 7: QUALITY ASSURANCE/ QUALITY CONTROL</b> .....	2-49
14.1 Introduction .....	2-50
14.2 Experimental Objectives .....	2-50
14.3 QA/QC Work Plan .....	2-50
14.3.1 Daily QA/QC Verifications.....	2-51
14.3.2 QA/QC Verifications Performed Every Two Weeks .....	2-51
14.3.3 QA/QC Verifications Performed Every Testing Period .....	2-50

## TABLE OF CONTENTS (continued)

	<b><u>Page</u></b>
14.4 On-Site Analytical Methods.....	2-51
14.4.1 pH .....	2-50
14.4.2 Turbidity .....	2-51
14.4.2.1 Bench-Top Turbidimeters .....	2-51
14.4.2.2 In-Line Turbidimeters .....	2-51
14.4.3 Temperature.....	2-52
14.4.4 Dissolved Oxygen.....	2-52
14.5 Chemical Samples Shipped Off-Site for Analysis .....	2-52
14.5.1 Organic Samples .....	2-52
14.5.2 Inorganic Samples.....	2-52
14.5.3 SOC Analysis.....	2-53
14.6 Trip Control.....	2-54
 <b>15.0 TASK 8: COST EVALUATION.....</b>	 <b>2-55</b>
 <b>16.0 SUGGESTED READING.....</b>	 <b>2-57</b>

## TABLES

Table 3.1	Example Statements of Performance Capabilities for SOC Removal .....	2-8
Table 9.1	NF Membrane Pretreatment Data.....	2-31
Table 9.2	Daily Operations Log Sheet for a Two-Stage Membrane Pilot Plant .....	2-32
Table 9.3	Operating and Water Quality Data Requirements for Membrane Processes .....	2-34
Table 10.1	Water Quality and Analytical Methods .....	2-36
Table 12.1	NSF Operations and Maintenance Manual Criteria - NF Membrane Process Package Plants.....	2-42
Table 12.2	Requirements for Maintenance and Operability of NF Membrane Process Package Plants .....	2-44
Table 12.3	NF Membrane Plant Design Criteria Reporting Items .....	2-45
Table 12.4	NF Membrane Element Characteristics .....	2-46
Table 15.1	Design Parameters for Cost Analysis .....	2-55
Table 15.2	Operations and Maintenance Costs .....	2-56

## FIGURE

Figure 9.1	Sample Locations for a Two-Stage Membrane Process.....	2-33
------------	--	------

## LIST OF APPENDICES

<b>APPENDIX A - SOC HEALTH EFFECTS INFORMATION .....</b>	<b>2-59</b>
<b>APPENDIX B – PROPOSED SOC<sub>s</sub> FOR REGULATION .....</b>	<b>2-61</b>

## LIST OF ABBREVIATIONS

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DIC	dissolved inorganic carbon
EPA	Environmental Protection Agency
FOD	Field Operations Document
FTO	Field Testing Organization
GAC	granular activated carbon
HF	hollow fiber
HSD	homogeneous solution diffusion model
IMS	Integrated Membrane Systems
IOC	inorganic compounds
MCL	maximum contaminant level
MCLG	maximum contaminant level goal
MF	microfiltration
MFI	modified fouling index
MTC	mass transfer coefficient
MWCO	molecular weight cut-off
NF	nanofiltration
NPDES	National Pollutant Discharge Elimination System
O&M	operation and maintenance
PEG	polyethylene glycol
QA/QC	Quality Assurance/Quality Control
RO	reverse osmosis
SCADA	Supervisory Control and Data Acquisition
SDI	silt density index
SDWA	Safe Drinking Water Act
SOC	synthetic organic chemical
SW	surface water
TFC™	thin-film composite
TOC	total organic carbon
TDS	total dissolved solids
UF	ultrafiltration
WTP	water treatment plant

---

## 1.0 APPLICATION OF THIS NSF EQUIPMENT VERIFICATION TESTING PLAN

This document is the NSF Equipment Testing Verification Plan (Plan) for evaluation of membrane processes to be used within the structure provided by NSF's *"Protocol for Equipment Verification Testing for the Removal of Synthetic Organic Chemical Contaminants by Packaged and/or Modular Drinking Water Treatment Systems"*. This Plan is to be used as a guide in the development of the Field Operations Document (FOD) for testing of membrane process equipment to achieve removal compliance of synthetic organic chemical contaminants (SOCs).

In order to participate in the equipment verification process for membrane processes, the equipment Manufacturer and their designated Field Testing Organization (FTO) shall employ the procedures and methods described in this test plan and in the referenced NSF Protocol Document as guidelines for the development of a FOD. The FTO shall clearly specify in its FOD the SOCs targeted for removal and sampling program that shall be followed during Verification Testing. The FOD should generally follow the Verification Testing Tasks outlined herein, with changes and modifications made for adaptations to specific membrane equipment. At a minimum, the format of the procedures written for each Task in the FOD should consist of the following sections:

- Introduction
- Objectives
- Work Plan
- Analytical Schedule
- Evaluation Criteria

The primary treatment goal of the equipment employed in this Verification Testing program is to remove SOCs present in water supplies such that permeate waters are in compliance with Phase II and V of the Safe Drinking Water Act (SDWA), as well as, proposed maximum contaminant levels (MCLs) listed in Drinking Water Regulations and Health Advisories (USEPA 1996). Therefore, experimental design of the FOD shall be developed so that relevant performance specifications for membrane process related to SOC removal are addressed. The Manufacturer may wish to establish a Statement of Performance Capabilities (Section 3.0 General Approach) that is based upon removal of target SOCs from feedwaters, or alternatively established one based upon compliance with drinking water standards. For example, the Manufacturer could include in the FOD a Statement of Performance Capabilities that would achieve compliance with maximum contaminant levels (MCLs) stipulated in the National Primary Drinking Water Standards or the EPA National Secondary Drinking Water Regulations for a specific water quality parameter. The experimental design of the FOD shall be developed to address the specific Statement of Performance Capabilities established by the Manufacturer. Each FOD shall include all of the included tasks, Tasks 1 to 9.

## 2.0 INTRODUCTION

Membrane processes are currently in use for a number of water treatment applications ranging from removal of inorganic constituents; total dissolved solids (TDS), total organic carbon (TOC), synthetic organic chemicals (SOCs), radionuclides and other constituents.

In order to establish appropriate operations conditions such as permeate flux, recovery, cross-flow velocity, the Manufacturer may be able to apply some experience with his equipment on a similar water source. This may not be the case for suppliers with new products. In this case, it is advisable to require a pre-test optimization period so that reasonable operating criteria can be established. This would aid in preventing the unintentional but unavoidable optimization during the Verification Testing. The need of pre-test optimization should be carefully reviewed with NSF, the FTO and the Manufacturer early in the process.

Pretreatment processes ahead of RO systems are generally required to remove particulate material and to ensure provision of high quality water to the membrane systems. For example, RO membranes cannot generally be applied to treatment of surface waters without pretreatment of the feedwater to the membrane system. For surface water applications, appropriate pretreatment, primarily for removal of particulate and microbiological species, must be applied as specified by the Manufacturer. In the design of the FOD, the Manufacturer shall stipulate which feedwater pretreatments are appropriate for application upstream of the RO membrane process. The stipulated feedwater pretreatment process(es) shall be employed for upstream of the membrane process at all times during the Equipment Verification Testing Program.

### **3.0 GENERAL APPROACH**

Testing of equipment covered by this Verification Testing Plan will be conducted by an NSF-qualified FTO that is selected by the equipment Manufacturer. Analytical water quality work to be carried out as a part of this Verification Testing Plan will be contracted with a laboratory certified by a State or accredited by a third-party organization (i.e., NSF) or the U.S. Environmental Protection Agency (USEPA) for the appropriate water quality parameters.

For this Verification Testing, the Manufacturer shall identify in a Statement of Performance Capabilities the specific performance criteria to be verified and the specific operational conditions under which the Verification Testing shall be performed. The Statement of Performance Capabilities must be specific and verifiable by a statistical analysis of the data. Statements should also be made regarding the applications of the equipment, the known limitations of the equipment and under what conditions the equipment is likely to fail or underperform. There are different types of Statements of Performance Capabilities that may be verified in this testing. Examples include two statements shown in Table 3.1.

During Verification Testing, the FTO must demonstrate that the equipment is operating at a steady-state prior to collection of data to be used in verification of the Statement of Performance Capabilities. For each Statement of Performance Capabilities proposed by the FTO and the Manufacturer in the FOD, the following information shall be provided:

- percent removal of the targeted SOC;
- rate of treated water production (i.e., flux);
- recovery;
- feedwater quality regarding pertinent water quality parameters;
- temperature;
- concentration of target SOC; and



- other pertinent water quality and operational conditions.

This NSF Equipment Verification Testing Plan is broken down into 9 tasks, as shown in the Section 6.0, Overview of Tasks. These Tasks shall be performed by any Manufacturer wanting the performance of their equipment verified by NSF. The Manufacturer's designated FTO shall provide full detail of the procedures to be followed in each Task in the FOD. The FTO shall specify the operational conditions to be verified during the Verification Testing Plan. All permeate flux values shall be reported in terms of temperature-corrected flux values, as either gallons per square foot per day (gfd) at 77 °F or liters per square meter per hour (L/(m<sup>2</sup>-hr) at 25 °C.

**Table 3.1: Example Statements of Performance Capabilities for SOC Removal**

<b>Type of Statement of Performance Capabilities</b>	<b>Example of Statement of Performance Capabilities</b>
<b>SOC Removal</b>	This packaged plant is capable of achieving 98percent removal of the SOC chlordane 60-day operation period at a flux of 15 gpm/sf (75 percent recovery; temperature between 20 and 25 °C) in feedwaters with chlordane concentrations less than 0.1 µg/L and total dissolved solids concentrations less than 500 mg/L.
<b>Regulatory Compliance</b>	This packaged plant is capable of producing a product water meeting the National Primary Drinking Water Standards for chlordane concentration during a 60-day operation period at a flux of 15 gpm/sf (75 percent recovery; temperature between 20 and 25 °C) in feedwaters with chlordane concentrations less than 0.1 µg/L and total dissolved solids concentrations less than 500 mg/L.

## 4.0 BACKGROUND

This section provides an overview of the literature review related to SOC regulations, health effects and contaminant removal by membrane processes and membrane system design. These items will assist in recognizing the vast number of SOC contaminants, identifying the ability to remove SOC's from water supplies using membrane processes, defining membrane systems and describing the mechanisms that will help in qualifying and quantifying the removal efficiency of the membrane process tested.

### 4.1 Regulatory and Health Effects

Since the passage of the Safe Drinking Water Act of 1974 (SDWA) requiring the establishment of recommended maximum contaminant levels (MCLs) for compounds that are deemed undesirable for consumption in public water supplies. Since that time there has been a growing awareness of the need for the control and removal of organic and inorganic contaminants from potable drinking water supplies. At the time of the passage of the SDWA of 1974, there were more than 12,000 chemical compounds known to be in commercial use. Many of these synthetic compounds are finding their way into potable water sources and ultimately into finished drinking water.

Within the past decade, several hundred specific organic chemicals have been identified in minute amounts in various drinking water supplies in the United States and abroad. Although at the present time the specific cause(s) of cancer are little understood, many of these commercially used organic compounds have been found to cause both acute and chronic adverse health effects in humans at various exposure levels. Therefore, in order to minimize risks to human health, the exposure levels to these compounds must be reduced to the lowest level possible that is both technologically and economically feasible.

The chronic health hazards associated with the presence of SOC's in drinking water have become a major concern of United States governmental agencies in more recent times. Consequently, contamination of potable water by SOC's is a significant national problem. Phase II and V of the SDWA have promulgated MCLs for 32 SOC's, of which 15 have been identified as carcinogenic. Appendix A lists the MCL, source of contamination and potential health effects for each regulated SOC. In addition, Appendix B lists the 46 SOC's proposed in the Drinking Water Regulations and Health Advisories and the Federal Register to be considered for regulation (USEPA 1996, 1997).

## **4.2 SOC Removal by Membrane Processes**

This NSF Equipment Verification Testing Plan is applicable to any pressure-driven membrane process used to achieve removal of SOC's. Furthermore, this testing plan is applicable to spiral-wound (SW) and hollow-fiber (HF) membrane configurations.

Membrane processes have been shown to be highly effective for the removal of SOC's. However, removal is a function of membrane mass transfer coefficients (MTCs), flux, recovery and feed concentration and will be expected to vary by membrane type. RO is also effective in producing a better overall quality of water.

Some advantages to the use of membrane processes for the removal of SOC's include:

- a small space requirement;
- removal of contaminant ions, dissolved solids, bacteria, and particles; and
- relative insensitivity to flow and TDS levels, and low effluent concentration.

Disadvantages include:

- higher capital and operating costs;
- higher level of pretreatment required;
- possible membrane fouling; and
- large reject streams.

Pressure-driven membrane processes are currently in use for a broad number of water treatment applications including the removal of pesticides and herbicides (i.e. SOC's), natural organic matter (NOM) which contributes to disinfection by-product formation, dissolved minerals, radionuclides and microbial contaminants such as *Giardia* and *Cryptosporidium*. Typically, higher pressure membrane applications such as nanofiltration (NF) and reverse osmosis (RO) are capable of removing SOC's, as well as ions contributing to hardness.

In contrast, low-pressure membrane processes, such as microfiltration (MF) and ultrafiltration (UF) are typically employed to provide a physical barrier for removal of microbial and particulate contaminants from drinking waters. However, the MF and UF membrane processes have not been shown to be effective for removal of SOC's unless another unit operation such as granular activated or powdered activated carbon is employed.

Suppliers of drinking water are subject to stringent government regulations for potable water quality regarding allowable pesticide and herbicide (i.e. SOC's) concentrations. In particular, European standards require less than 0.1 µg/L for any one particular pesticide or herbicide and no greater than 0.5 µg/L for total pesticides and herbicides in drinking water. Many investigators have shown that RO/NF are effective techniques for pesticide and herbicide removal (Duranceau 1992, Camp 1995, Takigawa et.al. 1995, and Kruithof et.al. 1995). However, specific mechanisms underlying SOC rejection are largely unknown. In the paragraphs to follow, results from published accounts of pesticide reduction and the inferences regarding suspected mechanisms for removal are presented.

It has been demonstrated that membrane processes are effective for SOC removal (Duranceau and Taylor 1992, and Hofman et.al. 1993). However the mechanisms for SOC removal are still under investigation and are a subject of research. Intensive research efforts have investigated the associated rejection mechanisms for various pesticides and herbicides. Included among these mechanisms are:

- size exclusion,
- steric hindrance (shape)
- electrostatic repulsion
- adsorption
- matrix effects

In general, uncharged pesticide and herbicide rejection by RO/NF has been observed to decrease with decreasing molecular size (i.e. molecular weight or molecular cross-sectional area) (Kruithof et.al 1995, Chen et.al 1997, and Berg and Gimbel 1997). Since molecular weight and molecular cross-sectional area are not always directly related, distinguishing between these two parameters is an important consideration for determination of a size exclusion rejection mechanism for uncharged SOC's (Berg and Gimbel 1997).

A study where NF treatability of a mixture of Elbe River (Germany) water and ground water with high sulfate and hardness content spiked with trace amounts of several SOC's ( $C_{\text{feed}} \approx 1 \mu\text{g/L}$ ) was conducted with both flat-sheet membrane films and spiral wound elements. Simazine, atrazine, terbutylazine, diuron, metazachlorine, TCA, and mecoprop composed the pesticide "cocktail" with which the surface water was spiked. Rejection of uncharged species terbutylazine, atrazine and simazine were reported to be in order of increasing size (Berg and Gimbel 1997). With the only difference between these species being the number of methyl groups, terbutylazine, with three methyl groups, was the highest rejected. Atrazine being the next largest in size was better rejected than simazine. Charged organic species were found to be significantly more rejected (predominately >85% for all membranes) by the negatively charged membranes than the polar SOC's despite substantial size differences. However, a combination of both electrostatic repulsion and size was suspected to influence rejection as demonstrated by higher rejection of the

SOC mecoprop as compared to its smaller charged counterpart TCA. By adjusting the feed pH to 3, added insight was provided by analyzing the rejections of mecoprop in its dissociated and undissociated form. These results showed greater rejection for the dissociated form of mecoprop. The rejection of the undissociated form was less than in its dissociated form and was comparable to the rejection of uncharged diuron, which suggested a removal mechanism for these non-polar species to be that of steric hindrance.

Additional flat-sheet testing has been performed to evaluate the effects of matrix conditions upon pesticide rejection as applied to different membrane polymers. Reported evaluations (Chen et.al. 1997) have demonstrated general pesticide rejection in order of highest to lowest by membrane film to be polyamide, amine, and cellulose acetate based polymers. This conclusion resulted from an overall assessment of pesticides commonly used in both the U.S and Europe and their rejection in separate distilled, inorganic, organic and inorganic-organic matrices. These pesticides included simazine, atrazine, cyanazine, bentazone, diuron, DNOC, pirimicarb, metamitron, metribuzin, MCPA, mecoprop, and vinchlozolin at feed concentrations of approximately 10 µg/L. These investigators also demonstrated that solvent properties, inorganic versus organic in particular, did not have a large influence upon SOC rejection. The order of pesticide rejection by matrix listed in order of increasing to decreasing rejection of pesticides was reported to be inorganics, organics, distilled water and combination of inorganic and organic. Among all four matrices, overall rejection varied by less than 10%. While the flat-sheet film tests were able to detect significant performance differences among cellulose acetate versus thin-film composite membranes, “finite differences (using similar types of membranes) were not detected using cell tests because of variations in membrane films due to manufacturing or analytical limitations.”

SOC removal has also been the focus of attention for several Dutch Utilities. The PWN Water Supply Company of North Holland has studied cellulose acetate membrane polymers as applied to surface water for over 15 years (Camp 1995). Joint research between PWN and KIWA has shown thin-film composite (TFC) membranes to have better rejection properties than cellulose acetate (CA) membranes, but have the disadvantage of being more prone to fouling when surface water sources are used. As a single barrier, CA membranes were demonstrated to be inadequate for pesticide removal and they recommend granular activated carbon (GAC) post treatment (Kruithof et.al. 1995). However, at PWN, TFC membranes were shown to reject 90 to 95% of applied pesticide cocktails while CA membranes offered, as expected, less rejection of the SOC's. Moreover, chlorophenols were removed 25 to 90% with CA membranes. Experiments conducted in Leiduin, the Netherlands also showed significant pesticide rejection. Using a 4-2-1 array equipped with six 4" single elements, Toray SU 710 L type membranes achieved 97 to greater than 99% rejection for all pesticides except 2,4 dichlorophenol (50%) and diuron (87%). Specifically, the highly rejected SOC's in this mixture were atrazine (99%), bentazone (>99%), DNOC (97%), and isoproturon (97%) with feed concentrations ranging from 5.1 to 6.3 µg/L. Bench-scale experiments conducted at PWN, which compared Hydranautics CPA2 and Toray SU 710 L, revealed comparable pesticide rejection for the two composite membranes. The least rejected SOC's were diuron and simazine of the trace concentration SOC mixture that included atrazine, bentazone, and DNOC. However, each individual SOC was rejected at or greater than 96% by both membranes except for diuron as treated by the Toray SU 710 L single element.

## 4.3 Membrane System Design Considerations

Conventional NF or RO membrane systems consist of pretreatment, membrane processing and post-treatment. These processes are discussed in the following sections.

### 4.3.1 Pretreatment

The purpose of pretreatment is to control and minimize membrane fouling and reduce flux decline. The conventional pretreatment process consists of scale inhibitor (anti-scalant) and/or acid addition in combination with microfiltration. These pretreatment process are used to control scaling and protect the membrane elements; they are required for conventional RO or NF membrane systems. The membranes can be fouled or scaled during operation. Fouling is caused by particulate materials such as colloids and organics that are present in the raw water attaching to the membrane surface, and will reduce the productivity of the membrane. Scaling is caused by the precipitation of a sparingly soluble salt within the membrane because of the solute concentration exceeding solubility. If a raw water is excessively fouling, additional or advanced pretreatment is required.

Flux decline indicated by a reduction in membrane process productivity can be a result of scaling, colloidal fouling, microbiological fouling and organic chemical fouling. Scaling can be approximated by chemical analysis and equilibrium calculations. Fouling indices can approximate colloidal fouling. Microbiological and organic chemical fouling can only be approximated at this time by pilot testing. These mechanisms should be recognized and understood, and are presented below in order to develop strategies to control flux decline.

**4.3.1.1 Scaling.** In an RO/NF membrane process, salts present in the feedwater are concentrated on the feed side of the membrane. This concentration process continues until saturation and salt precipitation (scaling) occurs. Scaling will reduce membrane productivity, and consequently, will limit the rate of water that may be recovered as permeate on a sustained basis. The maximum recovery is the recovery at which the limiting salt first begins to precipitate.

Limiting salts can be identified from the solubility products of potential limiting salts in the raw feedwater. Since ionic strength increases on the feed side of the membrane, the effect of ionic strength upon the solubility products must also be considered and taken into account for these calculations. Some limiting salts may be controlled via the addition of acid or scale inhibitor or both to the feedwater prior to membrane treatment. Typical sparingly soluble salts that may limit recovery in pressure-driven membrane processes include, but are not limited to,  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ,  $\text{CaF}_2$  and  $\text{SiO}_2$ .

As the feedwater passes through the membrane element from the feed side to the concentrate end of the membrane system, and the permeate water is removed, the feedwater salts become more concentrated. For instance, in a 75% recovery membrane system, the concentrate contains almost four times the concentration of salts that were present in the feedwater. This is called concentration polarization. Concentration polarization is the term used to describe the increased salt concentration that occurs at the surface of the membrane elements. As the permeate water passes through the membrane,

the concentration of the rejected salts build up on the high-pressure side of the membrane surface. The amount of increased salt concentration over the bulk stream depends on how quickly the salts diffuse back into the bulk stream.

A high salt concentration at the membrane surface results in an increase in salt passage through the membrane. The increase in local salt concentration can lead to saturation of solution components resulting in precipitation on the membrane surface.

**4.3.1.2 Colloidal Fouling.** Colloidal fouling results from particles that exist in the influent which buildup on the surface of the membrane. The build-up forms a cake, which eventually is compressed and reduces flow through the membrane. Initially, cake formation does not significantly reduce productivity. However, after the cake compresses, the productivity decreases and the compressed cake must be removed. MF or UF membranes can be backwashed to remove the cake. However, spiral-wound RO and NF membranes require chemical cleaning to remove the cake. Advanced pretreatment processes such as cross-flow MF and multi-media filtration should control colloidal fouling.

**4.3.1.3 Microbiological Fouling.** Microbiological fouling results from biological growth in the membrane element, which results in a reduction in membrane productivity or an increase in pressure drop through an element. No reliable methods have been demonstrated for prediction of biofouling. Microbiological growth can occur in the feed spacers or on the membrane surface. Microbiological growth will occur in membranes, but this growth does not always result in significant productivity loss. Advanced pretreatment processes may aid in the control of microbiological fouling.

**4.3.1.4 Chemical Fouling.** Chemical fouling results from the interaction of dissolved solutes in the feed stream with the membrane surface, which results in a reduction in membrane productivity. Chemical interaction between solute and the membrane surface will occur to some degree, but membrane productivity may not be reduced. Advanced pretreatment processes may aid in the control of chemical fouling.

#### **4.3.2 Advanced Pretreatment**

Advanced pretreatment would include unit operations that precede scaling control and cartridge filtration. By definition, unit operations that precede conventional pretreatment would be advanced pretreatment. Examples of advanced pretreatment would be coagulation/flocculation/sedimentation, oxidation followed by greensand filtration, continuous cross-flow microfiltration, multi-media filtration, and granular activated carbon (GAC) filtration.

#### **4.3.3 Membrane Processes**

The membrane process follows pretreatment. The majority of dissolved contaminants are removed in the membrane process. If the membrane scales or fouls, the productivity of the membrane system declines and eventually the membranes must be chemically cleaned to restore productivity. Cleaning frequencies for RO or NF systems average about 6 months when treating ground waters (Taylor et.al. 1990) and can be as low as 1 to 2 weeks when treating surface water with integrated membrane systems (IMSs).

UF or MF membranes as a stand alone process cannot remove SOC. However, powdered activated carbon (PAC) can be used for SOC adsorption followed by UF or MF to remove the PAC from the flow stream. MF and UF membranes are sieving controlled and do not have a low enough molecular weight cut-off (MWCO) range to reject many of the known SOC or inorganic compounds (IOC). RO and NF membranes can achieve significant SOC rejection because the MWCO of these membranes are low and many SOC cannot pass (Duranceau 1992). This is also the case with IOC and radionuclides. Although RO and NF have been shown to be among the most promising processes for SOC and IOC removal, not all SOC or IOC are rejected by these processes. RO and NF membranes use both sieving and diffusion mechanisms to reject SOC and IOC from drinking water and rejection will increase as the MW and charge of the contaminant increases. Typically, charged solutes and solutes with MWCOs greater than 200 mg/mmol are highly rejected by RO and NF.

UF and MF membranes do not affect corrosivity because inorganic ions are not removed; however, RO and NF do remove inorganic solutes from water, and this can impact the corrosivity of the permeate water.

#### **4.3.4 Post-Treatment**

Typical post-treatment unit operations can consist of disinfection, aeration, stabilization and storage. Aeration may be required to strip dissolved gases (Duranceau 1993). Stabilization may be required to produce a non-corrosive finished water since membrane permeate can be corrosive. Alkalinity recovery is an effective process for recovering dissolved inorganic carbon (DIC) in the permeate. Alkalinity can be recovered by lowering the pH prior to membrane filtration converting the alkalinity to CO<sub>2</sub>, and then raising the pH of the permeate in a closed system to recover dissolved CO<sub>2</sub> as alkalinity. Bypassing feedwater and blending it with membrane permeate is another way of stabilizing the finished water; however, blending would negate the benefit of the membrane treatment system to act as a physical barrier against microbial contaminants.

#### **4.3.5 Waste Disposal**

In addition to post treatment, the concentrate stream from the membrane processes must be treated and/or disposed of in some manner. Although membrane processes are at present often technically and economically well suited to produce drinking water, the disposal of membrane concentrate will become more difficult and more expensive because of increased regulation. Effective concentrate disposal methods depend on the concentrate water quality, local regulations and site-specific factors (AWWARF 1993). The handling and disposal of the wastes generated by treatment technologies removing SOC from drinking water pose concerns to the water supplier, to local and State governments and to the public at large. The potential handling hazards associated with SOC warrant the development of a viable membrane concentrate disposal method. Information regarding concentrate disposal options can be found in Membrane Concentrate Disposal (AWWARF 1993). The document investigates the application of regulations to the disposal of membrane concentrate. The document first addresses membrane concentrate and its characteristics, including the definitions and natures of the wastes that are being generated. Then the disposal methods that are being regulated are addressed, including descriptions of how to dispose of the concentrate. Finally, the



regulations and permits that apply to the various disposal options are addressed. The following are disposal options that must be approved by the State or local government prior to implementation of a waste disposal program.

#### Liquid Waste Disposal

- Direct discharge into storm sewers or surface water.
- Discharge into sanitary sewer.
- Deep well injection.
- Drying or chemical precipitation.

#### Solid Waste Disposal

- Temporary lagooning (surface impoundment).
- Disposal in landfill.
- Disposal without prior treatment.
  - a) With prior temporary lagooning.
  - b) With prior mechanical dewatering.
  - c) Application to land (soil spreading/conditioning).
- Disposal at State licensed waste facility.

## **5.0 DEFINITION OF OPERATIONAL PARAMETERS**

The following terms are presented here for subsequent reference in this test plan:

**Array** – An array is the series flow stream configuration of pressure vessels through a train defined by stages (4:2:1 array).

**Bulk Rejection** - Percent solute concentration retained by the membrane relative to the bulk stream concentration.

$$1 - \frac{C_p}{C_f}$$

where:

$C_f$  = feedwater concentration of specific constituent (mg/L)

$C_p$  = permeate concentration of specific constituent (mg/L)

**Bulk Solution** - The solution on the high-pressure side of the membrane that has a water quality between that of the influent and concentrate streams.

**Cleaning Frequency** - The loss or decrease of the mass transfer coefficient (MTC) for water measures membrane productivity over time of production. Membranes foul during operation. Constant production is achieved in membrane plants by increasing pressure. Cleaning is done



when the pressure increases by 10 to 15 percent. Cleaning frequency (CF) and a measurement of productivity can be determined from the MTC decline.

$$CF = \frac{\Omega K_w}{\frac{dK_w}{dt}}$$

where:

CF = cleaning frequency (days)

$\Omega$  = acceptable rate of MTC loss

$dK_w/dt$  = rate of MTC decline (gsfd/psi-d)

**Concentrate ( $Q_c$ ,  $C_c$ )** - One of the membrane output streams that has a more concentrated water quality than the feed stream.

**Conventional RO/NF Process** - A treatment system consisting of acid and/or scale inhibitor addition for scale control, cartridge filtration, RO/NF membrane filtration, aeration, chlorination and corrosion control.

**Feed ( $Q_f$ ,  $C_f$ )** - Input stream to the membrane process after pretreatment.

**Feedwater** - Water introduced to the membrane module.

**Field Operations Document (FOD)** - A written document of procedures for on-site/in-line testing, sample collection, preservation, and shipment and other on-site activities described in the USEPA/NSF Protocol(s) and Test Plan(s) that apply to a specific make and model of a package plant/modular system.

**Field Testing Organization (FDO)** - An organization qualified to conduct studies and testing of package plants or modular systems in accordance with protocols and test plans. The role of the field testing organization is to complete the application on behalf of the Company; to enter into contracts with NSF, as discussed herein; and arrange for or conduct the skilled operation of a package plant during the intense periods of testing during the study and the tasks required by the Protocol.

**Flux ( $F_w$ )** - Mass (lb/ft<sup>2</sup>-day) or volume (gal/ft<sup>2</sup>-day, gsfd, gfd) rate of transfer through membrane surface.

$$F_w = K_w [\Delta P - \Delta \Pi] = \frac{Q_p}{A}$$

where:

$F_w$  = water flux (M/L<sup>2</sup>·t)

$K_w$  = global water mass transfer coefficient (t<sup>-1</sup>)

$\Delta P$  = transmembranic pressure gradient (M/L<sup>2</sup>)

$\Delta \Pi$  = osmotic pressure gradient (M/L<sup>2</sup>)

$Q_p$  = permeate flow (L<sup>3</sup>/t)

A = membrane surface area ( $L^2$ )

**Fouling** - Reduction of productivity measured by a decrease in the temperature normalized water MTC.

**Fouling Indices** - Fouling indices are simple measurements that provide an estimate of the required pretreatment for membrane processes. Fouling indices are determined from membrane tests and are similar to mass transfer coefficients for membranes used to produce drinking water. Fouling indices can be quickly developed from simple filtration tests, are used to qualitatively estimate pretreatment requirements and possibly could be used to predict membrane fouling. The silt-density index (SDI), modified fouling index (MFI) and mini plugging factor index (MPFI) are the most common fouling indices. The SDI, MFI and the MPFI are defined using the basic resistance model, and are quantitatively related to water quality and NF membrane fouling.

Some approximations for required indices prior to conventional membrane treatment are given below (Sung et. al. 1994).

**Fouling Index Approximations for NF**

<b>Fouling Index</b>	<b>Range</b>
SDI	< 3
MFI	< 10 s/L <sup>2</sup>

Silt-Density Index (SDI): The SDI is the most commonly used test to predict a water's potential to foul a membrane by colloidal particles smaller than 0.45 microns. SDI is only a guide for pretreatment and is not an indication of adequate pretreatment. The SDI is a static measurement of resistance, which is determined by samples taken at the beginning and the end of the test. The SDI test is performed by timing the anaerobic hydraulic flow through a 47 mm diameter, 0.45 micron membrane filter at a constant pressure of 30 psi. The time required for 500 mL of the feedwater to pass through the filter is measured when the test is first initiated, and is also measured at time intervals of 5, 10, and 15 minutes after the start of the test. The value of the SDI is then calculated as follows (ASTM D-4189-82).

$$SDI = \left[ \frac{1 - \frac{t_i}{t_f}}{t_T} \right] (100\%)$$

where:

$t_i$  = time to collect initial 500 mL sample

$t_f$  = time to collect 500 mL sample at time  $t = T$

$t_T$  = total running time of the test; 5, 10, or 15 minutes.

If the index is below a value of 3 then the water should be suitable for reverse osmosis. If the SDI is below 3, the impact of colloidal fouling is minimized.

**Modified Fouling Index (MFI):** The MFI is determined using the same equipment and procedure used for the SDI, except that the volume is recorded every 30 seconds over a 15 minute filtration period (Schipper and Verdouw 1980). The development of the MFI is consistent with Darcy's Law in that the thickness of the cake layer formed on the membrane surface is assumed to be directly proportional to the filtrate volume. The total resistance is the sum of the filter and cake resistance. The MFI is defined graphically as the slope of an inverse flow verses cumulative volume curve as shown in the following equations

$$\frac{dV}{dt} = \frac{\Delta P}{\mu} \frac{A}{(R_f + R_k)}$$

$$t = \frac{\mu V R_f}{\Delta P A} + \frac{\mu V^2 I}{2 \Delta P A^2}$$

$$\frac{1}{Q} = (a + MFI)V$$

where:

$R_f$  = resistance of the filter

$R_k$  = resistance of the cake

$I$  = measure of the fouling potential

$Q$  = average flow (liters/second)

$a$  = constant

Typically the cake formation, build-up and compaction or failure can be seen in three distinct regions on a MFI plot. The regions corresponding to blocking filtration and cake filtration represent productive operation, whereas compaction would be indicative of the end of a productive cycle.

**Hollow-Fiber** – Fine hollow fibers of membrane material are extruded in either a cellulose triacetate or a polyamide. The ends of the fibers are sealed in an epoxy block connected with the outside of the housing. The epoxy block is cut to allow the flow from the inside of the fine fibers to the other side of the epoxy block, where it is collected. The pressurized feedwater passes across the outside of the fibers. Pure water permeates the fibers and is collected at the end of the element.

The hollow-fiber housings are capable of holding a large quantity of fibers, this allowing a single element to produce a large permeate flow rate. Hollow-fiber elements are typically used for seawater desalination, and for brackish-water applications

**Influent** - Input stream to the membrane array after the recycle stream has been blended with the feed stream. If there is no concentrate recycle then the feed and influent streams are identical.

**Mass Transfer Coefficient (MTC) ( $K_w$ )** - Mass or volume unit transfer through membrane based on driving force (gfd/psi).

$$K_w = \frac{Q_p}{A(\Delta P - \Delta \Pi)}$$

where:

$K_w$  = global water mass transfer coefficient ( $t^{-1}$ )

$\Delta P$  = transmembranic pressure gradient ( $M/L^2$ )

$\Delta \Pi$  = osmotic pressure gradient ( $M/L^2$ )

$Q_p$  = permeate flow ( $L^3/t$ )

$A$  = membrane surface area ( $L^2$ )

**Membrane Element** - A single membrane unit containing a bound group of spiral wound or hollow-fiber membranes to provide a nominal surface area for treatment.

**Membrane Molecular Weight Cutoff Determination** - The membrane molecular weight cutoff (MWCO) of membranes is commonly used to characterize membrane rejection capability. Membrane MWCO is typically determined by measuring the rejection of different molecular weight nonionic polymers. Solute rejection is defined as:

$$\% \text{ Solute Rejection} = \left( 1 - \frac{C_p}{C_f} \right) (100\%)$$

Given the narrow molecular weight bands of polyethylene glycol (PEG) solutions, these nonionic random coil polymers can be applied to membranes for MWCO estimation. Although the percent PEG rejection varies by manufacturer, 80 to 90 percent PEG rejection has been used. Neither the percent rejection nor the material is fixed except by membrane manufacturer. The standard molecular weight solutions can be measured as TOC and correlated to PEG concentration. This correlation can then be applied for assessment of PEG rejection by the membrane and subsequent MWCO determination.

**Membrane Productivity** - Membrane productivity will be assessed by the rate of mass transfer coefficient ( $MTC_w$ ) decline over time of operation. As flux declines, a constant product can be achieved by increasing pressure to maintain a constant flux.

Net Driving Pressure (NDP): The net driving pressure (NDP) is calculated using the influent, concentrate and permeate pressure.

$$NDP = \left[ \frac{(P_f + P_c)}{2} \right] - P_p - \Delta \Pi$$

where:

NDP = net driving pressure for solvent transport across the membrane (psi, bar)

$P_f$  = feedwater pressure to the feed side of the membrane (psi, bar)

$P_c$  = concentrate pressure on the reject side of the membrane (psi, bar)

$P_p$  = permeate pressure on the treated water side of the membrane (psi, bar)

$\Delta \pi$  = osmotic pressure (psi)

Osmotic Pressure Gradient ( $\Delta\pi$ ):: The term osmotic pressure gradient refers to the difference in osmotic pressure generated across the membrane barrier as a result of different concentrations of dissolved salts. In order to determine the NDP, the osmotic pressure gradient must be estimated from the influent, concentrate and permeate TDS.

$$\Delta\pi = \left( \left[ \frac{(TDS_f + TDS_c)}{2} \right] - TDS_p \right) \left( \frac{1 \text{ psi}}{100 \frac{\text{mg}}{\text{L}}} \right)$$

where:

$TDS_f$  = feedwater total dissolved solids (TDS) concentration (mg/L)

$TDS_c$  = concentrate TDS concentration (mg/L)

$TDS_p$  = permeate TDS concentration (mg/L)

Mass Transfer Coefficient ( $MTC_w$ ): The  $MTC_w$  is calculated by dividing the permeate flow by the membrane surface area.

$$F_w = \frac{Q_p}{A} = (MTC_w)(NDP)$$

From this the  $MTC_w$  can be calculated. However, given the relationship between temperature and the viscosity of water, flux should be normalized to a standard temperature condition (25°C). These relationships should be provided by the membrane manufacturer and used to normalize the flux data set as shown below.

$$MTC_{w, 25^\circ C} = \frac{F_{w, 25^\circ C}}{NDP}$$

Temperature Adjustment for Flux Calculation: If manufacture does not specify a temperature correction equation the following equation may be used so that water production can be compared on an equivalent basis.

$$F_{w, 25^\circ C} = F_{w, T^\circ C} \left( 1.03^{(25^\circ C - T^\circ C)} \right)$$

Recovery: Recovery should also be calculated using the permeate and influent flow.

$$R = \frac{Q_p}{Q_i}$$

Using the above equations the  $MTC_w$ , normalized flux and recovery for each stage and the system can be calculated for each set of operational data and plotted as a function of cumulative operating time.

**Package Plant** - A complete water treatment system including all components from the connection to the raw water(s) intake through discharge to the distribution system.

**Permeate ( $Q_p$ ,  $C_p$ )** - The membrane output stream that has convected through the membrane.

$$Q_p C_p = Q_f C_f - Q_c C_c$$

**Permeate** - Water produced by the membrane process.

**Permeate Flux** - The average permeate flux is the flow of permeate divided by the surface area of the membrane. Permeate flux is calculated according to the following formula:

$$J_t = \frac{Q_p}{S}$$

where:

$J_t$  = permeate flux at time  $t$  (gfd, L/(h-m<sup>2</sup>))

$Q_p$  = permeate flow (gpd, L/h)

$S$  = membrane surface area (ft<sup>2</sup>, m<sup>2</sup>)

It should be noted that only gfd and L/(h-m<sup>2</sup>) shall be considered acceptable units of flux for this testing plan.

**Pressure Vessel** - A single tube or housing that contains several membrane elements in series.

**Raw** - Input stream to the membrane process prior to any pretreatment.

**Recovery** - The recovery of feedwater as permeate water is given as the ratio of permeate flow to feedwater flow:

$$\% \text{ System Recovery} = \left[ \frac{Q_p}{Q_f} \right] (100\%)$$

where:

$Q_f$  = feedwater flow to the membrane (gpm, L/h)

$Q_p$  = permeate flow (gpm, L/h)

**Recycle Ratio ( $r$ )** - The recycle ratio represents the ratio of the total flow of water that is used for cross-flow and the net feedwater flow to the membrane. This ratio provides an idea of the recirculation pumping that is applied to the membrane system to reduce membrane fouling and specific flux decline.

$$\text{Recycle Ratio} = \left[ \frac{Q_r}{Q_f} \right]$$

where:

$Q_f$  = feedwater flow to the membrane (gpm, L/h)

$Q_r$  = recycle hydraulic flow in the membrane element (gpm, L/h)

**Rejection (mass)** – The mass of a specific solute entering a membrane system that does not pass through the membrane.

$$\left(1 - \frac{Q_p C_p}{Q_f C_f}\right)$$

**Scaling Control** - Controlling precipitation or scaling within the membrane element requires identification of a limiting salt, acid addition for prevention of  $\text{CaCO}_3$  and/or addition of a scale inhibitor. The limiting salt determines the amount of scale inhibitor or acid addition. A diffusion controlled membrane process will concentrate salts on the feed side of the membrane. If excessive water is passed through the membrane, this concentration process will continue until a salt precipitates and scaling occurs. Scaling will reduce membrane productivity and consequently recovery is limited by the allowable recovery just before the limiting salt precipitates. The limiting salt can be determined from the solubility products of potential limiting salts and the actual feed stream water quality. Ionic strength must also be considered in these calculations as the natural concentration of the feed stream during the membrane process increases the ionic strength, allowable solubility and recovery.

Calcium carbonate scaling is commonly controlled by sulfuric acid addition however sulfate salts are often the limiting salts. Commercially available scale inhibitors can be used to control scaling by complexing the metal ions in the feed stream and preventing precipitation. Equilibrium constants for these scale inhibitors are not available which prevents direct calculation. However some manufacturers provide computer programs for estimating the required scale inhibitor dose for a given recovery, water quality and membrane. The following are general equations for the solubility products and ionic strength approximations.

**Solubility Product:** Calculation of the solubility product of selected sparingly soluble salts will be important exercise for the test plan in order to determine if there are operational limitations caused by the accumulation of limiting salts at the membrane surface. Text book equilibrium values of the solubility product should be compared with solubility values calculated from the results of experimental Verification Testing, as determined from use of the following equation:

$$K_{sp} = \gamma_A^x [A^{y-}]^x \gamma_B^y [B^{x+}]^y$$

where:

$K_{sp}$  = solubility product for the limiting salt being considered

$\gamma$  = free ion activity coefficient for the ion considered (i.e., A or B)

[A] = molal solution concentration of the anion A for sparingly soluble salt  $A_x B_y$

[B] = solution concentration of the anion B

x, y = stiochiometric coefficients for the precipitation reaction of A and B

**Mean Activity Coefficient:** The mean activity coefficients for each of the salt constituents may be estimated for the concentrated solutions as a function of the ionic strength:

$$\log \gamma_{A,B} = -0.509 Z_A Z_B \sqrt{\mu}$$

where:

$\gamma$  = free ion activity coefficient for the ion considered (i.e., A or B)

$Z_A$  = ion charge of anion A

$Z_B$  = ion charge of cation B

$\mu$  = ionic strength

**Ionic Strength:** A simple approximation of the ionic strength can be calculated based upon the concentration of the total dissolved solids in the feedwater stream:

$$\mu = (2.5 \cdot 10^{-5})(\text{TDS})$$

where:

$\mu$  = ionic strength

TDS = total dissolved solids concentration (mg/L)

**Solute** - The dissolved constituent (mg/L) in a solution or process stream.

**Solute Rejection** - Solute rejection is controlled by a number of operational variables that must be reported at the time of water sample collection. Bulk rejection of a targeted inorganic chemical contaminant may be calculated by the following equation.

$$\% \text{ Solute Rejection} = \left[ \frac{C_f - C_p}{C_f} \right] (100\%)$$

where:

$C_f$  = feedwater concentration of specific constituent (mg/L)

$C_p$  = permeate concentration of specific constituent (mg/L)

**Solvent** - A substance, usually a liquid such as water, capable of dissolving other substances.

**Solvent and Solute Mass Balance** - Calculation of solvent mass balance is performed to verify the reliability of flow measurements through the membrane. Calculation of solute mass balance across the membrane system is performed to estimate the concentration of limiting salts at the membrane surface.

$$Q_f = Q_p + Q_c$$

$$Q_f C_f = Q_p C_p + Q_c C_c$$

where:

$Q_f$  = feedwater flow to the membrane (gpm, L/h)

$Q_p$  = permeate flow (gpm, L/h)



$Q_c$  = concentrate flow (gpm, L/h)

$C_f$  = feedwater concentration of specific constituent (mg/L)

$C_p$  = permeate concentration of specific constituent (mg/L)

$C_r$  = concentrate concentration of specific constituent (mg/L)

**Specific Flux** - At the conclusion of each chemical cleaning event and upon return to membrane operation, the initial condition of transmembrane pressure shall be recorded and the specific flux calculated. The efficiency of chemical cleaning shall be evaluated by the recovery of specific flux after chemical cleaning as noted below, with comparison drawn from the cleaning efficiency achieved during previous cleaning evaluations. Comparison between chemical cleanings shall allow an evaluation of irreversible fouling. Two primary indicators of cleaning efficiency and restoration of membrane productivity will be examined in this task.

Percent Recovery of Specific Flux: The immediate recovery of membrane productivity, as expressed by the ratio between the final specific flux ( $F_{sf}$ ) and the initial specific flux ( $F_{si}$ ) measured for the subsequent run.

$$\% \text{ Recovery of Specific Flux} = \left[ 1 - \frac{F_{sf}}{F_{si}} \right] (100\%)$$

where:

$F_{sf}$  = Specific flux (gfd/psi, L/(h-m<sup>2</sup>)/bar) at end of run (final)

$F_{si}$  = Specific flux (gfd/psi, L/(h-m<sup>2</sup>)/bar) at beginning of run (initial).

Percent Loss of Original Specific Flux: The loss of original specific flux capabilities, as expressed by the ratio between the initial specific flux for any given filtration run ( $F_{si}$ ) divided by the original specific flux ( $F_{sio}$ ), as measured at the initiation of the first filtration run in a series.

$$\% \text{ Loss of Original Specific Flux} = \left[ 1 - \frac{F_{si}}{F_{sio}} \right] (100\%)$$

**Spiral-Wound** - Spiral-wound membrane elements are constructed of flat sheet membranes folded and glued on three edges to create several membrane envelopes. The open edge of the each envelope is glued to a central collection pipe with perforations to allow water from inside the envelope to pass into the pipe. The envelopes are spun around the central collection pipe. Layered inside each envelope is a thin layer of fabric that prevents the envelope from sealing itself off when the outside of the envelope is exposed to high pressure. The fabric allows the passage of permeate water to the center collection tube.

The feed water enters the end of the spiral-wound element and moves across the surface of the rolled-up membrane envelopes. Spacers between the envelopes promote turbulence so that pure water permeates the envelopes, any salts left behind will diffuse back into the bulk solution. Inside the envelope the pressure is near atmospheric, whereas the pressure on the feedwater side can be as high as 1,000 psi. The pressure differential drives the pure water into the membrane envelope. In the envelope the permeate passes through fabric material and finds its way into the

central collection pipe. The water in the collection pipe travels to the end where it either enters the collection tube of another element, or is transferred to the permeate port of the end cap of the housing.

**Stage** – A stage is the configuration of an array.

**Train** – A train is a parallel flow stream through the membrane system. For instance a 5 MGD membrane system may be comprised of five 1 MGD trains.

**Verification Statement** - A written document that summarizes a final report reviewed and approved by NSF on behalf of the USEPA or directly by the USEPA.

**Water System** - The water system that operates using packaged water treatment equipment to provide potable water to its customers.

## 6.0 OVERVIEW OF TASKS

This Plan is applicable to the testing of package water treatment equipment utilizing membrane processes. Testing of membrane processes will be conducted by a NSF-qualified Testing Organization that is selected by the Manufacturer. Water quality analyses will be performed by a State, NSF, or EPA qualified analytical laboratory. This Plan provides objectives, work plans, schedules, and evaluation criteria for the required tasks associated with the equipment testing procedure.

The following is a brief overview of the tasks that shall be included as components of the Verification Testing Program and FOD for removal of SOCs.

- **Task 1: Characterization of Raw Water** – Obtain chemical, biological and physical characterization of the raw water. Provide a brief description of the watershed that provides the raw water to the water treatment plant.
- **Task 2: Membrane Productivity** - Demonstrate operational conditions for the membrane equipment; permeate water recovery achieved by the membrane equipment; and rate of flux decline observed over an extended membrane process operation.
- **Task 3: Finished Water Quality** – Evaluate the water quality produced by membrane processes as it relates to raw water quality and operational conditions.
- **Task 4: Cleaning Efficiency** – Evaluate the effectiveness of chemical cleaning to the membrane system and confirm that the Manufacturer-recommended cleaning practices are sufficient to restore membrane productivity.
- **Task 5: Operations and Maintenance (O&M)** - Develop an O&M manual for each system submitted. The O&M manual shall characterize membrane process design, outline a membrane process cleaning procedure or procedures, and provide a concentrate disposal plan.
- **Task 6: Data Collection and Management** – Establish an effective field protocol for data management between the Field Testing Organization and NSF.
- **Task 7: Quality Assurance / Quality Control (QA/QC)** – Develop a QA/QC protocol for Verification Testing. This is an important item that will assist in obtaining an accurate

measurement of operational and water quality parameters during membrane equipment Verification Testing.

- **Task 8: Cost Evaluation** - Develop capital and O&M costs for the submitted NF membrane technology and package plant.

## 7.0 TESTING PERIODS

The required tasks of the NSF Equipment Verification Testing Plan (Tasks 1 through 9) are designed to be completed over a 60-day period, not including mobilization, shakedown and start-up. The schedule for equipment monitoring during the 60-day testing period shall be stipulated by the FTO in the FOD, and shall meet or exceed the minimum monitoring requirements of this testing plan. The FTO shall ensure in the FOD that sufficient water quality data and operational data will be collected to allow estimation of statistical uncertainty in the Verification Testing data, as described in the “*Protocol for Equipment Verification Testing of for Removal of Synthetic Organic Chemical Contaminants*”. The FTO shall therefore ensure that sufficient water quality and operational data is collected during Verification Testing for the statistical analysis described herein.

For membrane process treatment equipment, factors that can influence treatment performance include:

- Feedwaters with high seasonal concentrations of inorganic constituents and TDS. These conditions may increase finished water concentrations of inorganic chemical contaminants and may promote precipitation of inorganic materials in the membrane;
- Feedwaters with variable pH; increases in feedwater pH may increase the tendency for precipitation of sparingly soluble salts in the membrane module and may require variable strategies in anti-scalant addition and pH adjustment;
- Cold water, encountered in winter or at high altitude locations;
- High concentrations of natural organic matter (measured as TOC), which may be higher in some waters during different seasonal periods;
- High turbidity, often occurring in spring, as a result of high runoff resulting from heavy rains or snowmelt.

It is highly unlikely that all of the above problems would occur in a water source during a single 60-day period during the Verification Testing Program. Membrane testing conducted beyond the required 60-day testing may be used for fine-tuning of membrane performance or for evaluation of additional operational conditions. During the testing periods, evaluation of cleaning efficiency and finished water quality can be performed concurrent with membrane operation testing procedures.

During the time intervals between equipment verification runs, the package water treatment equipment may be used for production of potable water. If the equipment is being used for the production of potable water, routine operation for water production is expected. In addition, the equipment should not be used for potable water production should a finished water quality parameter not comply with the requirements of the National Primary Drinking Water Standards or the EPA National Secondary Drinking Water Regulations. The operating and water quality

data collected and furnished to the local regulatory agency should also be supplied to the NSF-qualified FTO. If package water treatment equipment is operated for potable water production, the data supplied to the FTO shall be evaluated with regard to compliance with National Primary Drinking Water Standards or EPA National Secondary Drinking Water Regulations.

## **8.0 TASK 1: CHARACTERIZATION OF RAW WATER**

### **8.1 Introduction**

A characterization of raw water quality is needed to determine if the concentrations of SOC's or other raw water contaminants are appropriate for the use of NF membrane processes. The feedwater quality can influence the performance of the equipment as well as the acceptance of testing results by Federal and State regulatory agencies.

### **8.2 Objectives**

One reason for performing a raw water characterization is to obtain at least one-year of historical raw water quality data from the raw water source. The objective is to:

- demonstrate seasonal effects on the concentration of SOC's;
- develop maximum and minimum concentrations for the contaminant; and
- develop a probable percentage of removal necessary to meet the proposed MCL.

If historical raw water quality is not available, a raw water quality analysis of the proposed feedwater shall be performed prior to equipment Verification Testing.

### **8.3 Work Plan**

The characterization of raw water quality is best accomplished through the performance of laboratory testing and the review of historical records. Sources for historical records may include municipalities, laboratories, USGS (United States Geographical Survey), USEPA, and local regulatory agencies. If historical records are not available preliminary raw water quality testing shall be performed prior to equipment Verification Testing. The specific parameters of characterization will depend on the NF membrane process that is being tested. The following characteristics should be reviewed and documented:

- |                        |              |             |
|------------------------|--------------|-------------|
| • Specific SOC         | • True Color | • Nitrate   |
| • Temperature          | • Chloride   | • Sodium    |
| • pH                   | • Fluoride   | • Potassium |
| • TDS/Conductivity     | • Sulfate    | • Strontium |
| • Total Hardness       | • Ammonia    | • Phosphate |
| • Calcium Hardness     | • Iron       | • SDI       |
| • Total Organic Carbon | • Manganese  | • MFI       |
| • Total Alkalinity     | • Silica     |             |

- Turbidity
- Barium

Data collected should reflect seasonal variations in the above data if applicable. This will determine variations in water quality parameters that will occur during Verification Testing. The data that is collected will be shared with NSF so that the FTO can determine the significance of the data for use in developing a test plan. If the raw water source is not characterized, the testing program may fail, or results of a testing program may not be considered acceptable. A description of the raw water source should also be included with the feedwater characterization. The description may include items such as:

- size of watershed;
- topography;
- land use;
- nature of the water source; and
- potential sources of pollution.

#### **8.4 Schedule**

The schedule for compilation of adequate water quality data will be determined by the availability and accessibility of historical data. The historical water quality data can be used to determine the suitability of NF membrane processes for the treatment for the raw source water. If raw water quality data is not available, a preliminary raw water quality testing should be performed prior to the Verification Testing of the NF membrane equipment.

#### **8.5 Evaluation Criteria**

The feedwater quality shall be evaluated in the context of the Manufacturer's Statement of Performance Capabilities for the removal of SOCs. The feedwater should challenge the capabilities of the chosen equipment, but should not be beyond the range of water quality suitable for treatment by the chosen equipment. For NF membrane processes, a complete scan of water quality parameters may be required in order to determine limiting salt concentrations, necessary for establishing pretreatment criteria.

### **9.0 TASK 2: MEMBRANE PRODUCTIVITY**

#### **9.1 Introduction**

The removal of SOCs from drinking water supplies is accomplished by NF membrane filtration. The effectiveness of NF membrane processes for SOC removal will be evaluated in this task. Membrane mass transfer coefficient, flux and recovery will be evaluated in this task. After installation of a NF membrane, compaction and ripening of the membrane will cause a characteristic flux decline with time until the membrane stabilizes. After this initial flux decline, the rate of flux decline will be used to demonstrate membrane performance for the specific operating conditions to be verified. The operational conditions to be verified shall be specified by the Manufacturer in terms of a temperature-corrected flux (normalized flux) value (e.g., gsf/d at 77°F or L/(m<sup>2</sup>hr) at 25°C) before the initiation of the Program.

Flux decline is a function of water quality, membrane type, configuration and operational conditions. In establishing the range of operation for the membrane performance evaluations, limiting salt information should be used to define the run scenarios. The run conditions should include operating scenarios, which approach and exceed these projected limits. Subsequent water quality analysis will allow for assessment of the degree of saturation of the sparingly soluble salts in the final concentrate. The degree of saturation of the salts should then be compared to resulting membrane productivity decline. Table 9.1 presents an example of membrane pretreatment data required to provide baseline conditions and assist in evaluating membrane productivity.

Some Manufacturers may wish to employ the NF membrane process with a pretreatment process in order to reduce flux decline and improve removal of SOC's. Any pretreatment included in the membrane treatment system that is designed for removal of SOC's shall be considered an integral part of the packaged membrane treatment system and shall not be tested independently. In such cases, the system shall be considered as a single unit and the pretreatment process shall not be separated for optional evaluation purposes.

## **9.2 Experimental Objectives**

The objectives of this task are to demonstrate:

- Operational conditions for the membrane equipment;
- Permeate water recovery achieved by the membrane equipment; and
- Rate of flux decline observed over extended membrane process operation.

Raw water quality shall be measured prior to system operation and then monitored every two weeks during the 60-day testing period at a minimum. It should be noted that the objective of this task is not process optimization, but rather verification of membrane operation at the operating conditions specified by the Manufacturer, as it pertains to permeate flux and transmembrane pressure, and SOC removal.

## **9.3 Work Plan**

Determination of ideal membrane operating conditions for a particular water may require as long as one year of operation. For this task the Manufacturer shall specify the operating conditions to be evaluated in this Verification Testing Plan and shall supply written procedures on the operation and maintenance of the membrane treatment system. The Manufacturer shall evaluate flux decline. The Manufacturer shall also determine the limiting salt and identify possible foulants and scalants, and use this for performance evaluation for their particular membrane equipment. The set of operating conditions shall be maintained for the 60-day testing period (24-hour continuous operation). The Manufacturer shall specify the primary permeate flux at which the equipment is to be verified. Additional operating conditions can be verified in separate 60-day testing periods.

After set-up and "shakedown" of membrane equipment, membrane operation should be established at the flux condition to be verified. Testing of additional operational conditions could be performed by extending the number of 60-day testing periods beyond the initial 60-day

period required by the Verification Testing Program at the discretion of the Manufacturer and their designated FTO.

Additional 60-day periods of testing may also be included in the Verification Testing Plan in order to demonstrate membrane performance under different feedwater quality conditions. For membrane processes, extremes of feedwater quality (e.g., low temperature, high TOC concentration, variable SOC concentrations, high SDI and high turbidity) are the conditions under which membranes are most prone to fouling and subsequent failure. At a minimum the performance of the NF membrane equipment relative to SOC removal shall be documented during those periods of variable feedwater conditions. The Manufacturer shall perform testing with as many different water quality conditions as desired for verification status. Testing under each different water quality condition shall be performed during an additional 60-day testing period, as required above for each additional set of operating conditions.

The testing runs conducted under this task shall be performed in conjunction with finished water quality and if applicable, cleaning efficiency. With the exception of additional testing periods conducted at the Manufacturer's discretion, no additional membrane test runs are required for performance of cleaning efficiency and finished water quality. A continuous yearlong evaluation, although not required, may be of benefit to the Manufacturer for verification of long term trends.

### **9.3.1 Operational Data Collection**

Measurement of membrane feedwater flow and permeate flow (recycle flow where applicable) and system pressures shall be collected at a minimum of 3 eight-hour shifts per day. Table 9.2 is an example of a daily operational data sheet for a two-stage membrane system. This table is presented for informational purposes only. Figure 9.1 presents the sample locations for the daily operational data sheet. The actual forms will be submitted as part of the test plan and may be site-specific. Measurement of feedwater temperature to the membranes shall be made along with these three daily measurements in order to provide data for normalizing flux with respect to temperature

Water quality should be analyzed from the same locations identified for TDS in Table 9.2 prior to start-up and then twice a month for the parameters identified in Table 9.3, except for each SOC, which will be monitored weekly. Power costs for operation of the membrane equipment (pumping requirements, chemical usage, etc.) shall also be closely monitored and recorded by FTO during the 60-day testing period. Power usage shall be estimated by inclusion of the following details regarding equipment operation requirements: pumping requirements; size of pumps; name-plate; voltage; current draw; power factor; peak usage; etc. In addition, measurement of power consumption and chemical consumption shall be quantified by recording such items as day tank concentration, daily volume consumption and unit cost of chemicals.

### **9.3.2 Feedwater Quality Limitations**

The characteristics of feedwaters used during the 60-day testing period (and any additional 60-day testing periods) shall be explicitly stated in reporting the membrane flux and recovery data for each period. Accurate reporting of such feedwater characteristics are critical for the Verification Testing Program, as these parameters can

substantially influence the range of achievable membrane performance and treated water quality under variable raw water quality conditions. The following criteria and trends should also be presented in the Verification Testing Program:

- Evaluation criteria and minimum reporting requirements.
- Plot graph of SOC removed over time for each 30-day period of operation.
- Plot graph of NDP over time for each 30-day period of operation.
- Plot graph of TDS over time for each 30-day period of operation.
- Plot graph of  $F_{w25^{\circ}\text{C}}$  over time for each 30-day period of operation.
- Plot graph of  $\text{MTC}_w$  over time for each 30-day period of operation.
- Plot graph of recovery over time for each 30-day period of operation.

**TABLE 9.1: NF Membrane Pretreatment Data**

<b>Foulants and Fouling Indices of the Feedwater Prior to Pretreatment</b>	
Alkalinity (mg/L of $\text{CaCO}_3$ )	
Ca Hardness (mg/L of $\text{CaCO}_3$ )	
LSI	
Dissolved iron (mg/L)	
Total iron (mg/L)	
Dissolved aluminum (mg/L)	
Total aluminum (mg/L)	
Fluoride (mg/L)	
Phosphate (mg/L)	
Sulfate (mg/L)	
Calcium (mg/L)	
Barium (mg/L)	
Strontium (mg/L)	
Reactive silica (mg/L as $\text{SiO}_2$ )	
Turbidity (NTU)	
SDI	
<b>Pretreatment Processes Used Prior to Nanofiltration or Reverse Osmosis</b>	
Pre-filter listed pore size ( $\mu\text{m}$ )	
Type of acid used	
Acid concentration (units)	
mL of acid per L of feed	
Type of scale inhibitor used	
Scale inhibitor concentration (units)	

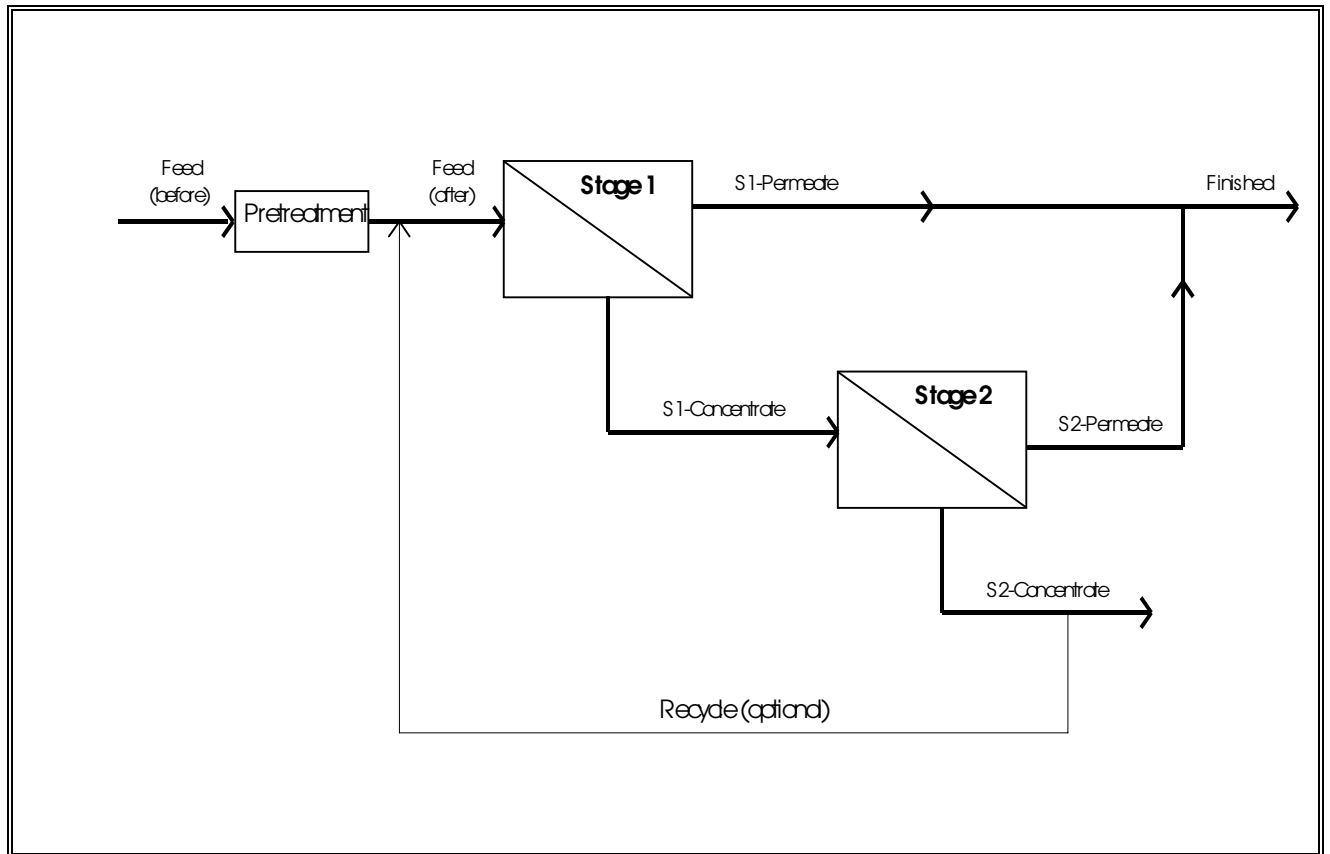


mL of scale inhibitor per L of feed	
Type of coagulant used	
Coagulant dose (mg/L)	
Type of polymer used during coagulation.	
Polymer dose (mg/L)	

**TABLE 9.2: Daily Operations Log Sheet for a Two-Stage Membrane Pilot Plant****Date:**

Parameter	Shift 1	Shift 2	Shift 3
<b>Time</b>			
<b>Initial</b>			
<b>Feed</b>			
$Q_{\text{feed}}$ (gpm)			
$\text{TDS}_{\text{feed}}$ (before pretreatment) (mg/L)			
$\text{TDS}_{\text{feed}}$ (after pretreatment) (mg/L)			
$P_{\text{feed}}$ (psi)			
$\text{pH}_{\text{feed}}$ (before pretreatment)			
$\text{pH}_{\text{feed}}$ (after pretreatment)			
$T_{\text{feed}}$ (°C)			
<b>Permeate - Stage 1</b>			
$Q_{\text{p-S1}}$ (gpm)			
$\text{TDS}_{\text{p-S1}}$ (mg/L)			
$P_{\text{p-S1}}$ (psi)			
<b>Concentrate - Stage 1</b>			
$Q_{\text{c-S1}}$ (gpm)			
$\text{TDS}_{\text{c-S1}}$ (mg/L)			
$P_{\text{c-S1}}$ (psi)			
$T_{\text{c-S1}}$ (°C)			
<b>Permeate - Stage 2</b>			
$Q_{\text{p-S2}}$ (gpm)			
$\text{TDS}_{\text{p-S2}}$ (mg/L)			
$P_{\text{p-S2}}$ (psi)			
<b>Concentrate - Stage 2</b>			
$Q_{\text{c-S2}}$ (gpm)			
$\text{TDS}_{\text{c-S2}}$ (mg/L)			
$P_{\text{c-S2}}$ (psi)			
<b>Finished</b>			
$Q_{\text{fin}}$ (gpm)			
$\text{TDS}_{\text{fin}}$ (mg/L)			
Recovery ( $Q_{\text{fin}}/Q_{\text{feed}}$ ) (%)			
<b>Recycle</b>			
$Q_{\text{recycle}}$ (gpm)			

**FIGURE 9.1: Sample Locations for a Two-Stage Membrane Process**



**TABLE 9.3: Operating and Water Quality Data Requirements for Membrane Processes**

<b>Parameter</b>	<b>Frequency and Importance for Sampling</b>
Feedwater Flow	3 * Daily (1)
Permeate Water Flow	3 * Daily (1)
Concentrate Water Flow	3 * Daily (1)
Feedwater Pressure	3 * Daily (1)
Permeate Water Pressure	3 * Daily (1)
Concentrate Water Pressure	3 * Daily (1)
List Each Chemical Used, And Dosage	Daily Data Or Monthly Average (1)
Hours Operated Per Day	Daily (1)
Hours Operator Present Per Day	Monthly Average (2)
Power Costs (Kwh/Million Gallons)	Monthly (2)
Independent check on rates of flow	Weekly (1)
Independent check on pressure gages	Weekly (2)
Verification of chemical dosages	Monthly (1)
SOCs	1, Weekly
Temperature	3 * Daily (1)
pH	3 * Daily (1)
TDS/Conductivity	3 * Daily (1)
Turbidity	Every two weeks (1)
True Color	Every two weeks (1)
Total Organic Carbon	Every two weeks (1)
UV Absorbance (254 nm)	Every two weeks (1)
Total Alkalinity	Every two weeks (1)
Total Hardness	Every two weeks (1)
Calcium Hardness	Every two weeks (1)
Sodium	Every two weeks (1)
Chloride	Every two weeks (1)
Iron	Every two weeks (1)
Manganese	Every two weeks (1)
Sulfate	Every two weeks (1)
Fluoride	Every two weeks (1)
Silica	Every two weeks (1)
Ammonia	Every two weeks (1)
Potassium	Every two weeks (1)
Strontium	Every two weeks (1)
Barium	Every two weeks (1)
Nitrate	Every two weeks (1)
TTHM	Every two weeks (2)
THAA	Every two weeks (2)
TOX	Every two weeks (2)

1 = Required 2 = Desired But Not Necessary

## **10.0 TASK 3: FINISHED WATER QUALITY**

### **10.1 Introduction**

Water quality data shall be collected for the raw and finished water as provided previously in Table 9.3. (Note, in some instances sampling concentrate water quality may be required because detection limits may be too low for a specified parameter.) At a minimum, the required sampling shall be one sampling at start-up and two sampling events per month while raw water samples are collected. Water quality goals and target removal goals for the membrane equipment should be proved and reported in the FOD.

### **10.2 Objectives**

The objective of this task is to verify the Manufacturer's claims. Table 9.3 presented a list of the minimum number of water quality parameters to be monitored during equipment Verification Testing has been provided in this document. The actual water quality parameters selected for testing and monitoring shall be stipulated in the FOD.

### **10.3 Work Plan**

The FOD shall identify the treated water quality objectives to be achieved in the Statement of Performance Capabilities of the equipment to be evaluated in the Verification Testing Program. The FOD shall also identify in the Statement of Performance Capabilities the specific SOC's that shall be monitored during equipment testing. The Statement of Performance Capabilities prepared by the FOD shall indicate the range of water qualities and operating conditions under which the equipment can be challenged while successfully treating the contaminated water supply.

It should be noted that many of the packaged and/or modular drinking water treatment systems participating in the SOC Removal Verification Testing Program will be capable of achieving multiple water treatment objectives. Although the SOC Verification Testing Plan is oriented towards removal of SOC's, the Manufacturer may want to look at the treatment system's removal capabilities for additional water quality parameters.

Many of the water quality parameters described in this task shall be measured on-site by the NSF-qualified FTO. A State, NSF or EPA qualified analytical laboratory shall perform analysis of the remaining water quality parameters. Representative methods to be used for measurement of water quality parameters in the field and lab are identified in Table 10.1. The analytical methods utilized in this study for on-site monitoring of raw and finished water qualities are described in Quality Assurance/ Quality Control (QA/QC). Where appropriate, the Standard Methods reference numbers and USEPA method numbers for water quality parameters are provided for both the field and laboratory analytical procedures.

For the water quality parameters requiring analysis at an off-site laboratory, water samples shall be collected in appropriate containers (containing necessary preservatives as applicable) prepared by the State, NSF or EPA qualified laboratory. These samples shall be preserved, stored, shipped and analyzed in accordance with appropriate procedures and holding times, including chain-of-custody requirements, as specified by the analytical lab.

**TABLE 10.1: Water Quality Analytical Methods**

<b>Parameter</b>	<b>Standard Method <sup>1</sup></b>	<b>EPA Method <sup>2</sup></b>
<b><u>Phase II SOCs</u></b>		
2,4,5-TP (Silvex)	6640 B	515.1; 515.2; 555
2,4-D (Formula 40, Weedar 64)	6640 B	515.1; 515.2; 555
Acrylamide		
Alachlor (Lasso)		505; 507; 525.2; 508.1
Aldicarb	6610 B	531.1
Aldicarb sulfone	6610 B	531.1
Aldicarb sulfoxide	6610 B	531.1
Atrazine		505; 507; 508.1; 525.2
Carbofuran (Furdan 4F)	6610 B	531.1
Chlordane	6410 B; 6630 B,C	505; 508; 508.1; 525.2
Dibromochloropropane (DBCP, Nemaflow))	6210 C,D; 6230 D; 6231 B	504.1; 551
Ethylene dibromide (EDB, Bromofume)		504.1; 551
Heptachlor (H-34, Heptox)	6410 B; 6630 B, C	505; 508; 508.1; 525.2
Heptachlor epoxide	6410 B; 6630 B, C	505; 508; 508.1; 525.2
Lindane	6630 B	505; 508; 508.1; 525.2
Methoxychlor (DMDT, Marlate)	6630 B	505; 508; 508.1; 525.2
Pentachlorophenol	6410 B; 6420 B; 6640 B	515.1; 515.2; 525.2; 555
Polychlorinated biphenyls (PCBs, Aroclor)	6410 B; 6630 C	505; 508; 508A
Toxaphene	6410 B; 6630 B, C	505; 508; 525.2
<b><u>Phase V SOCs</u></b>		
Adipate (diethylhexyl)		506; 525.2
Dalapon	6640 B	515.1; 552.1
Dichloromethane		
Dinoseb	6640 B	515.1; 515.2; 555
Dioxin		1613
Diquat		549.1
Endothall		548.1
Endrin	6410 B; 6630 B, C	505; 508; 508.1; 525.2

**TABLE 10.1: Water Quality Analytical Methods (Cont.)**

<b>Parameter</b>	<b>Standard Method <sup>1</sup></b>	<b>EPA Method <sup>2</sup></b>
Glyphosate	6651 B	547
Hexachlorobenzene	6040 B; 6410 B	505; 508; 508.1; 525.2
Hexachlorocyclopentadiene	6410 B	505; 508; 508.1; 525.2
Oxamyl (Vydate)	6610 B	531.1
Phthalate		506; 525.2
Phenanthrene (PAH)	6040 B; 6410 B; 6440 B	525.1; 550; 550.1
Picloram	6640 B	515.1; 515.2; 555
Simazine		505; 507; 508.1; 525.2
Trichlorobenzene (1,2,4-)	6040 B; 6210 D; 6220 C; 6230 D; 6410 B	
Trichloroethane (1,1,2,-)	6040 B; 6210 B, C, D; 6220 C; 6230 B, C, D	
<b><u>Physical Parameters</u></b>		
Temperature	2550 B	
pH	4500-H <sup>+</sup> B	150.1; 150.2
Conductivity	2510 B	120.1
Total Dissolved Solids	2540 C	
Total Suspended Solids	2540 D	
Turbidity	2130 B; Method 2	180.1
Dissolved Oxygen	4500-O B	
<b><u>Organics</u></b>		
True color	2120 B	
Total Organic Carbon	5310 C	
UV <sub>254</sub> absorbance	5910 B	
Total Trihalomethanes (TTHMs)	6232 B	524.3
Total Haloacetic Acids (THAAs)	6251 B	552.1
Total Organic Halogens (TOX)	5320 B	
<b><u>Inorganics</u></b>		
Total Alkalinity	2320 B	
Total Hardness	2340 C	

**TABLE 10.1: Water Quality Analytical Methods (Cont.)**

<b>Parameter</b>	<b>Standard Method <sup>1</sup></b>	<b>EPA Method <sup>2</sup></b>
Calcium Hardness	3500-Ca <sup>+2</sup> D	
Sodium	3111 B	200.7
Chloride	4110 B; 4500-Cl <sup>-</sup> D	300.0
Iron	3111 D; 3113 B; 3120 B	200.7; 200.8; 200.9
Manganese	3111 D; 3113 B; 3120 B	200.7; 200.8; 200.9
Sulfate	4110 B; 4500-SO <sub>4</sub> <sup>-2</sup> C, D, F	300.0; 375.2
Fluoride	4110 B; 4500-F <sup>-</sup> B, C, D, E	300.0
Silica (total and dissolved)	3120 B; 4500-Si D, E, F	200.7
Ammonia, NH <sub>3</sub>	4500-NH <sub>3</sub> B, C, D	350.3
Potassium	3111 B; 3500-K C, D, E	200.7
Strontium	3111 B; 3500-Sr C,D,E	200.7
Barium	3111 D; 3113 B; 3120 B	200.7; 200.8
Nitrate	4110 B; 4500-NO <sub>3</sub> <sup>-</sup> D, F	300.0; 353.2

1) AWWA, Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition, 1998.

2) EPA, Methods and Guidance for Analysis of Water, EPA 821-C-97-001, April 1997.

## **10.4 Analytical Schedule**

### **10.4.1 Removal of SOC's**

During the steady-state operation of each membrane testing period, SOC mass balances shall be performed on the membrane feed, permeate and concentrate water in order to determine the SOC removal capabilities of the membrane system.

### **10.4.2 Feed and Permeate Water Characterization**

At the beginning of each membrane testing period, the raw water, permeate and in some cases concentrate water shall be characterized at a single set of operating conditions by measurement of the water quality parameters identified in Table 9.3.

### **10.4.3 Water Quality Sample Collection**

Water quality data shall be collected at regular intervals during each period of membrane equipment testing. The minimum monitoring frequency for the required water quality parameters is once at start-up and weekly for SOC's and every two weeks for the remaining water quality parameters. The water quality sampling program may be expanded to include a greater number of water quality parameters and to require a greater frequency of parameter sampling. Analyses for organic water quality parameters shall be performed on water sample aliquots that were obtained simultaneously from the same



sampling location, in order to provide the maximum degree of comparability between water quality analytes.

No monitoring of microbial populations shall be required in this Equipment Verification Testing Plan. However, the Manufacturer may include optional monitoring of indigenous microbial populations to demonstrate removal capabilities.

#### **10.4.4 Raw Water Quality Limitations**

The characteristics of feedwaters encountered during each 60-day testing period shall be explicitly stated. Accurate reporting of such raw water characteristics such as those identified in Table 9.3 are critical for the Verification Testing Program, as these parameters can substantially influence membrane performance.

### **10.5 Evaluation Criteria and Minimum Reporting Requirements**

- Removal or reduction of SOC's.
- Water quality and removal goals specified by the Manufacturer.

## **11.0 TASK 4: CLEANING EFFICIENCY**

### **11.1 Introduction**

There are certain types of foulant scales that pose an immediate threat to the operational integrity of a membrane process. Examples of scale include calcium carbonate scale and silica or sulfate scale.

Should scaling or fouling occur during or following the test runs, the membrane equipment shall require chemical cleaning to restore membrane productivity. The number of cleaning efficiency evaluations shall be determined by the fouling frequency of the membrane during each specified test period. In the case where the membrane does not fully reach the operational criteria for fouling as specified by the Manufacturer, chemical cleaning shall be performed after the 30 days of operation, with a record made of the operational conditions before and after cleaning.

The membrane treatment process will be optimized for sustained production under high product water recovery and solvent flux. Productivity goals shall be stated in the FOD in terms of productivity decline and/or operational time.

Either normalized flux decline or solvent mass transfer (MTC<sub>w</sub>) reduction will determine productivity decline. The use of the normalized MTC<sub>w</sub> for productivity decline would eliminate the need for constant system pressure for productivity decline determination. Chemical cleaning of the membranes will be performed as necessary for the removal of reversible foulants per Manufacturer specifications. These cleaning events are to be documented and used as an aid in determining the nature of the fouling or scaling conditions experienced by the system. The cleaning solutions should also be analyzed to determine which constituents may have adsorbed or precipitated onto the membrane surface during cleaning. This may also prove useful for establishing the mechanism of removal for some SOC's.

## **11.2 Experimental Objectives**

The objective of this task is to evaluate the effectiveness of chemical cleaning to the membrane systems. The intent of this task is to confirm that standard Manufacturer-recommended cleaning practices are sufficient to restore membrane productivity for the systems under consideration. Cleaning chemicals and cleaning routines shall be based on the Manufacturer recommendations. This task is considered a "proof of concept" effort, not an optimization effort.

## **11.3 Work Plan**

The membrane systems may become fouled during the membrane test runs. These fouled membranes shall be utilized for the cleaning assessments herein. Each system shall be chemically cleaned using the recommended cleaning solutions and procedures specified by the Manufacturer, which will vary according to identified foulants or scale. After each chemical cleaning of the membranes, the system shall be restarted and then returned to the flux condition being tested.

The Manufacturer shall specify in detail the procedure(s) for chemical cleaning of the membranes. At a minimum, the following shall be specified:

- cleaning chemicals
- quantities and costs of cleaning chemicals
- hydraulic conditions of cleaning
- duration of each cleaning step
- chemical cleaning solution
- quantity and characteristics of residual waste volume to be disposed

## **11.4 Recommended Disposal Procedures**

Methods of disposal of membrane concentrate include, but are limited to the following:

- Public works wastewater plant;
- Deep well injection; or
- Discharge to a surface water with accordance to the National Pollutant Discharge Elimination System (NPDES) Program.

However SOC's are considered a potentially hazardous waste and the effluent must be monitored since it is concentrated. The concentrate disposal may require other State and/or Federal permits. In addition, a description of all cleaning equipment and its operation shall be described and included in the O&M manual.

## **11.5 Analytical Schedule**

### **11.5.1 Sampling**

The pH of each cleaning solution shall be determined and recorded during various periods of the chemical cleaning procedure. Conductivity and turbidity should also be used to monitor flush periods.

### **11.5.2 Operational Data Collection**

Flow and pressure data shall be collected before system shutdown due to membrane fouling; flow and pressure data shall also be collected after chemical cleaning.

## **12.0 TASK 5: OPERATIONS AND MAINTENANCE MANUAL**

An operations and maintenance (O&M) manual for the membrane system to be tested for SOC removal shall be included in the Verification Testing evaluation.

### **12.1 Objectives**

The objective of this task is to provide an O&M manual that will assist in operating, troubleshooting and maintaining the membrane system performance. The O&M manual shall:

- characterize the membrane process design;
- outline a membrane process cleaning procedure or procedures; and
- provide a concentrate disposal plan.

The concentrate disposal plan must be approved by the State in question for permanent installation. A fully developed concentrate disposal plan would be required because of the SOCs that have been concentrated in the waste stream. Criteria for evaluation of the equipment's O&M Manual shall be compiled and then evaluated and commented upon during verification by the FTO. An example is provided in Table 12.1.

Each specific test plan will include a list of criteria for evaluating O&M information. This shall be compiled and submitted for evaluation by USEPA, NSF and technical peer reviewers. An example is provided in Table 12.2. The purpose of this O&M information is to allow utilities to effectively choose a technology that their operators are capable of operating, and provide information on how many hours the operators can be expected to work on the system. Information about obtaining replacement parts and ease of operation of the system would also be valuable.

### **12.2 O&M Work Plan**

Descriptions for pretreatment, membrane process, and post-treatment to characterize the membrane system unit process design shall be developed. Membrane processes shall include the design criteria and membrane element characteristics. Examples of information required relative to the membrane design criteria and element characteristics are presented in Tables 12.3 and 12.4, respectively.

**TABLE 12.1: NSF OPERATIONS & MAINTENANCE MANUAL CRITERIA -  
NF Membrane Process Package Plants**

---

**MAINTENANCE:**

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The manufacturer should provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment such as:

- flow meters
- pressure gauges
- pumps
- motors
- valves
- chemical feeders
- mixers

The manufacturer should provide readily understood information on the recommended or required maintenance for non-mechanical or non-electrical equipment such as:

- membranes
  - pressure vessels
  - piping
- 

**OPERATION:**

---

The manufacturer should provide readily understood recommendation for procedures related to proper operation of the package plant equipment. Among the operating aspects that should be discussed are:

Chemical feeders:

- calibration check
- settings and adjustments - how they should be made
- dilution of chemicals and scale inhibitors - proper procedures

Monitoring and observing operation:

- mass balance calculations
- recovery calculation

**TABLE 12.1: NSF OPERATIONS & MAINTENANCE MANUAL CRITERIA -  
NF Membrane Process Package Plants (continued)**

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**OPERATION (continued):**

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Monitoring and observing operation (continued):

- pressure losses

The manufacturer should provide a troubleshooting guide; a simple check-list of what to do for a variety of problems including:

- flux decline;
- no raw water (feedwater) flow to plant;
- when the water flow rate through the package plant can not be measured;
- no chemical feed;
- automatic operation (if provided) not functioning;
- no electric power; and
- sand or silt entrainment (such as plugging of prefilters).

The following are recommendations regarding operability aspects of package plants membrane processes. These aspects of plant operation should be included if possible in reviews of historical data, and should be included to the extent practical in reports of package plant testing when the testing is done under the NSF Verification Program. During Verification Testing and during compilation of historical package plant operating data, attention shall be given to package plant operability aspects.

- are chemical feed pumps calibrated?
- are flow meters present and have they been calibrated?
- are pressure gauges calibrated?
- are pH meters calibrated?
- are TDS or conductivity meters calibrated?
- can cleaning be done automatically?
- can membrane seals be easily replaced?
- does remote notification occur (alarm) when pressure increases > 15% or flow drops > 15%?

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The reports on Verification Testing should address the above questions in the written reports. The issues of operability should be dealt with in the portion of the reports that are written in response to Operating Conditions and Treatment Equipment Performance, in the Membrane Process Test Plan.

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**TABLE 12.2: Requirements for Maintenance and Operability of  
NF Membrane Process Package Plants**

<b>MAINTENANCE INFORMATION</b>		
<b>Equipment</b>	<b>Maintenance Frequency</b>	<b>Replacement Frequency</b>
Membranes		
Pumps		
Valves		
Motors		
Mixers		
chemical mixers		
water meters		
pressure gauges		
cartridge filters		
Seals		
Piping		

<b>OPERABILITY INFORMATION: (rank from 1 (easy) to 3 (difficult), or N/A)</b>	
<b>Operation Aspect</b>	<b>Response</b>
Chemical feed pumps calibration	
Flow meters calibration	
Pressure gauges calibration	
pH meters calibration	
TDS or conductivity meters calibration	
Cleaning	
Replacement of membrane seals	
Measurement and control of flux decline	

<p><b>Notes:</b></p>          
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**TABLE 12.3: NF Membrane Plant Design Criteria Reporting Items**

<b>Parameter</b>	<b>Value</b>
Number of trains	
Number of stages	
Stage configuration	
Number of pressure vessels in stage 1	
Number of pressure vessels in stage 2	
Number of elements per pressure vessel	
Recovery per stage (%)	
Recovery for system (%)	
Design flow (gpm)	
Design temperature (°C)	
Design flux (gsfd)	
Surface area per element (ft <sup>2</sup> )	
MTC <sub>w</sub> (gsfd/psi)	
Maximum flow rate to an element (gpm)	
Minimum flow rate to an element (gpm)	
Pressure loss per element (psi)	
Pressure loss in stage entrance and exit (psi)	
Feed stream TDS (mg/L)	
SOC rejection (%) *	

\* Specify SOC name(s), chemical and trade name(s).

**TABLE 12.4: NF Membrane Element Characteristics**

Membrane manufacturer			
Membrane module model number			
Size of element used in study (e.g. 4" x 40")			
Active membrane area of element used in study			
Active membrane area of an equivalent 8" x 40" element			
Purchase price for an equivalent 8" x 40" element (\$)			
Molecular weight cutoff (Daltons)			
Membrane material / construction			
Membrane hydrophobicity (circle one)	Hydrophilic	Hydrophobic	
Membrane charge (circle one)	Negative	Neutral	Positive
Design pressure (psi)			
Design flux at the design pressure (gfd)			
Variability of design flux (%)			
MTC <sub>w</sub> (gfd/psi)			
Standard testing recovery (%)			
Standard testing pH			
Standard testing temperature (°C)			
Design cross-flow velocity (fps)			
Maximum flow rate to the element (gpm)			
Minimum flow rate to the element (gpm)			
Required feed flow to permeate flow rate ratio			
Maximum element recovery (%)			
Rejection of reference solute and conditions of test (e.g. solute type and concentration)			
Variability of rejection of reference solute (%)			
Spacer thickness (ft)			
Scroll width (ft)			
Acceptable range of operating pressures			
Acceptable range of operating pH values			
Typical pressure drop across a single element			
Maximum permissible SDI			
Maximum permissible turbidity (NTU)			
Chlorine/oxidant tolerance			
Suggested cleaning procedures			

Note: Some of this information may not be available, but this table should be filled out as completely as possible for each membrane tested.



The membrane treatment process will be optimized for sustained production under high product water recovery and solvent flux. Productivity goals shall be stated in the FOD.

Productivity decline will be indicated and signaled by either normalized flux decline or normalized solvent mass transfer ( $MTC_w$ ) reduction. Normalized means that the flux has been adjusted for temperature and pressure. The use of the normalized  $MTC_w$  for productivity decline would eliminate the need for constant system pressure for productivity decline determination.

Chemical cleaning of the membranes will be performed as necessary for the removal of reversible foulants per manufacturer specifications. These cleaning events are to be documented and used as an aid in determining the nature of the fouling or scaling conditions experienced by the system. The cleaning solutions could also be analyzed for determining which constituents may have adsorbed or precipitated onto the membrane surface. Analysis of cleaning solutions can be coupled with mass balances on the same solutes monitored during operation to determine solute accrual in membrane elements. This may prove useful for establishing the mechanism of removal for some SOCs. A cleaning efficiency evaluation is described in Section 11.0.

The potential handling hazards associated with SOCs warrant the development of a viable membrane concentrate disposal method and safety program. Provisions for concentrate disposal from the packaged and/or modular system must be developed as part of the work plan.

## **13.0 TASK 6: DATA COLLECTION AND MANAGEMENT**

### **13.1 Introduction**

The data management system used in the Verification Testing Program shall involve the use of computer spreadsheets, in addition to manual recording of operational parameters for the membrane processes on a daily basis.

### **13.2 Objectives**

The objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the FTO provides sufficient and reliable operational data to NSF for verification purposes. Chain-of-Custody protocols will be developed and adhered to.

### **13.3 Work Plan**

#### **13.3.1 Data Handling Work Plan**

The following protocol has been developed for data handling and data verification by the FTO. In addition to daily operational data sheets, a Supervisory Control and Data Acquisition (SCADA) system could be used for automatic entry of pilot-testing data into computer databases. Specific parcels of the computer database for operational and water quality parameters should then be downloaded by manual importation into electronic spreadsheets. These specific database parcels shall be identified based upon discrete time spans and monitoring parameters. In spreadsheet form, the data shall be manipulated into a convenient framework to allow analysis of membrane process operation. At a minimum, backup of the computer databases to diskette should be performed on a monthly basis.

Field testing operators shall record data and calculations by hand in laboratory notebooks for three eight-hour shifts per day. (Daily measurements shall be recorded on specially prepared data log sheets as appropriate. Table 9.2 presents an example of a daily log sheet) The laboratory notebook shall provide copies of each page. The original notebooks shall be stored on-site; the copied sheets shall be forwarded to the project engineer of the FTO at least once per week during the 60-day testing period. This protocol will not only ease referencing the original data, but offer protection of the original record of results. Pilot operating logs shall include

- descriptions of the and test runs;
- names of visitors; and
- descriptions of any problems.

Such descriptions shall be provided in addition to experimental calculations and other items.

### **13.3.2 Data Management**

The database for the project shall be set up in the form of custom designed spreadsheets. The spreadsheets shall be capable of storing and manipulating each monitored water quality and operational parameter from each task, each sampling location, and each sampling time. All data from the field laboratory analysis notebooks and data log sheets shall be entered into the appropriate spreadsheet. Data entry shall be conducted on-site by the designated field testing operators. All recorded calculations shall also be checked at this time.

Following data entry, the spreadsheet shall be printed and the printout shall be checked against the handwritten data sheet. Any corrections shall be noted on the hardcopies and corrected on the screen, and then the corrected recorded calculations will also be checked and confirmed. The field testing operator or engineer performing the data entry or verification step shall initial each step of the verification process.

Each experiment (e.g. each membrane process test run) shall be assigned a run number, which will then be tied to the data from that experiment through each step of data entry and analysis. As samples are collected and sent to State, NSF or EPA qualified laboratories, the data shall be tracked by use of the same system of run numbers. Data from the outside laboratories shall be received and reviewed by the FTO. These data shall be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

### **13.3.3 Statistical Analysis**

For the analytical data obtained during Verification Testing, 95 percent confidence intervals shall be calculated by the FTO for selected water quality parameters. The specific Plans shall specify which water quality parameters shall be subjected to the requirements of confidence interval calculation. As the name implies, a confidence interval describes a population range in which any individual population measurement

may exist with a specified percent confidence. When presenting the data, maximum, minimum, average and standard deviation should be included.

Calculation of confidence intervals shall not be required for equipment performance obtained during the equipment Verification Testing Program. In order to provide sufficient analytical data for statistical analysis, the FTO shall collect three discrete water samples at one set of operational conditions for each of the specified water quality parameters during a designated testing period.

## **14.0 TASK 7: QUALITY ASSURANCE/ QUALITY CONTROL**

### **14.1 Introduction**

Quality assurance and quality control (QAQC) of the operation of the membrane process equipment and the measured water quality parameters shall be maintained during the Equipment Verification Testing Program.

### **14.2 Experimental Objectives**

The objective of this task is to maintain strict QA/QC methods and procedures during the Equipment Verification Testing Program. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to verify exact conditions at the time of testing.

### **14.3 QA/QC Work Plan**

Equipment flow rates should be calibrated and verified and verification recorded on a routine basis. A routine daily walk through during testing shall be established to check that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to verify that chemicals are being fed at the defined flow rate, and into a flow stream that is operating at the expected flow rate. This will provide correct chemical concentrations in the flow stream. In-line monitoring equipment such as flow meters, etc. shall be checked as indicated below to verify that the readout matches with the actual measurement (i.e. flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

When collecting water quantity data, all system flow meters will be calibrated using the classic bucket and stopwatch method where appropriate. Hydraulic data collection will include the measurement of the finished water flow rate by the “bucket test” method. This would consist of filling a calibrated vessel to a known volume and measuring the time to fill the vessel with a stopwatch. This will allow for a direct check of the system flow measuring devices.

Mass balances will be performed on the system for water quality parameters measured in the feed, permeate and concentrate streams. This will enable an additional quality control check on the accuracy and reliability of the analyzed data. SOC's in particular will be analyzed in each process stream. However, the difficulty in measuring some low level SOC's may limit the mass balance to be calculated based on feed and concentrate. Mass balances may provide insight into the mechanism for rejection of individual SOC's. For example, mass balances showing

incomplete recovery for a particular SOC may suggest possible adsorption onto the membrane surface.

#### **14.3.1 Daily QA/QC Verifications**

- Chemical feed pump flow rates (check and verify components)
- On-line conductivity meters (check and verify components)
- On-line pH meters (standardize and recalibrate)
- On-line turbidimeter flowrates (verified volumetrically over a specific period of time)
- On-line turbidimeter readings checked against a properly calibrated bench model

#### **14.3.2 QA/QC Verifications Performed Every Two Weeks**

- Chemical feed pump flow rates (verify volumetrically over a specific time period)
- On-line conductivity meters (recalibrate)
- On-line flow meters/rotameters (clean equipment to remove any debris or biological buildup and verify flow volumetrically to avoid erroneous readings)

#### **14.3.3 QA/QC Verifications Performed Every Testing Period**

- Differential pressure transmitters (verify gauge readings and electrical signal using a pressure meter)
- Tubing (verify good condition of all tubing and connections, replace if necessary)

### **14.4 On-Site Analytical Methods**

Use of either bench-top field analytical equipment will be acceptable for the Verification Testing; however, on-line equipment is recommended for ease of operation. Use of on-line equipment is also preferable because it reduces the introduction of error and the variability of analytical results generated by inconsistent sampling techniques. However, standard and uniform calibration and standardization techniques that are approved should be employed. Table 10.1 lists Standard Methods and EPA methods of analysis.

#### **14.4.1 pH**

Analysis for pH shall be performed according to *Standard Method 4500-H<sup>+</sup>*. A 2-point calibration of the pH meter used in this study will be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in poorly buffered waters. Therefore, measure the pH under a continuous stream of sample by placing the tip of the probe in the sample container allowing the sample to overflow the container while the probe reaches equilibrium. If this is a problem, measurement of pH in a confined vessel is recommended to minimize the effects of carbon dioxide loss with the atmosphere.

## 14.4.2 Turbidity

Turbidity analyses shall be performed according to Standard Method 2130 or EPA Method 180.1 with either a bench-top or in-line turbidimeter. Grab samples shall be analyzed using a bench-top turbidimeter; readings from this instrument will serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of Verification Testing and on a weekly basis using primary turbidity standards of 0.1, 0.5 and 3.0 NTU. Secondary turbidity standards shall be used on a daily basis to verify calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

During each verification testing period, the bench-top and in-line turbidimeters will be left on continuously. Once each turbidity measurement is complete, the unit will be switched back to its lowest setting. All glassware used for turbidity measurements will be cleaned and handled using lint-free tissues to prevent scratching. Sample vials will be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The Field Testing Organization shall be required to document any problems experienced with the monitoring turbidity instruments, and shall also be required to document any subsequent modifications or enhancements made to monitoring instruments.

**14.4.2.1 Bench-Top Turbidimeters.** The method for collecting grab samples will consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity.

When cold water samples cause the vial to fog and prevent accurate readings, allow the vial to warm up by submersing partially into a warm water bath for approximately 30 seconds.

**14.4.2.2 In-Line Turbidimeters.** In-line turbidimeters may be used during verification testing and must be calibrated as specified in the manufacturer's operation and maintenance manual. It will be necessary to periodically verify the in-line readings using a bench-top turbidimeter; although the mechanism of analysis is not identical between the two instruments the readings should be comparable. Should these readings suggest inaccurate readings then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic verification of the sample flow should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. It should also be verified that the LED readout matches the data recorded on the data acquisition system, if the latter is employed.

### **14.4.3 Temperature**

Readings for temperature shall be conducted in accordance with *Standard Method 2550*. Raw water temperatures shall be obtained at least once daily. The thermometer shall have a scale marked for every 0.1 °C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST). (A thermometer having a range of -1°C to +51°C, subdivided in 0.1° increments, would be appropriate for this work.)

### **14.4.4 Dissolved Oxygen**

Analysis for dissolved oxygen shall be performed on raw ground water samples according to *Standard Method 4500-O* using an iodometric method or the membrane electrode method. The techniques described for sample collection must be followed very carefully to avoid causing changes in dissolved oxygen during the sampling event. Sampling for dissolved oxygen does not need to be coordinated with sampling for other water quality parameters, so dissolved oxygen samples should be taken at times when immediate analysis is going to be possible. This will eliminate problems that may be associated with holding samples for a period of time before the determination is made.

If the sampling probe is not mounted such that the probe is continuously exposed to the process stream, then care must be taken when measuring the dissolved oxygen concentration. For best results, collect the dissolved oxygen sample with minimal agitation and measure the dissolved oxygen concentration immediately. If possible, measure the dissolved oxygen under a continuous stream of sample by placing the tip of the probe in the sample container, allowing the sample to overflow the container while the probe reaches equilibrium (usually less than 5 minutes).

## **14.5 Chemical Samples Shipped Off-Site for Analysis**

The analytical methods that shall be used during testing for chemical samples that are shipped off-site for analyses are described in the section below.

### **14.5.1 Organic Samples**

Samples for analysis of total organic carbon (TOC), UV<sub>254</sub> absorbance, and dissolved organic carbon (DOC) shall be collected in glass bottles supplied by the state-certified or third party- or EPA-accredited laboratory and shipped at 4 °C to the analytical laboratory within 24 hours of sampling. These samples shall be preserved in accordance with Standard Method 5010 B. Storage time before analysis shall be minimized, according to Standard Methods.

### **14.5.2 Inorganic Samples**

Inorganic chemical samples shall be collected and preserved in accordance with Standard Methods or EPA-approved methods. The samples shall be refrigerated at approximately 2 to 8 °C. Samples shall be processed for analysis by a state-certified or third party- or

EPA-accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 2 to 8 °C until initiation of analysis.

### **14.5.3 SOC Analysis**

Analysis of SOC's requires a trained analyst using sophisticated instrumentation. Only state-certified or third party- or EPA-accredited laboratories shall analyze SOC samples that are collected during Initial Operations and Verification Testing. As stated in the "Protocol for Equipment Verification Testing of Synthetic Organic Contamination Removal," approved methods for some SOC's may not be available, and for these SOC's, a proposed, peer-reviewed method may be used.

There are many approved methods for analyzing Phase II and Phase V SOC's. Depending on the laboratory, gas chromatography (GC) or high performance liquid chromatography (HPLC) methods can be used to analyze SOC's. For both methods, the equipment is highly specialized and proper operation of these instruments requires a skilled laboratory technician.

Mass spectrometry is not required for all SOC's, however it is recommended for SOC identification. Retention times relative to the internal standard can also be used to identify SOC's. Either peak height or peak area can be used to determine the SOC concentrations.

SOC's shall be analyzed with an internal standard similar in analytical behavior and not affected by the matrix for QA/QC. An appropriate surrogate standard shall also be used during SOC analysis. Data pertaining to the internal and surrogate standards shall be reported with the SOC concentrations of the samples being analyzed. A method blank shall also be prepared and analyzed by the state-certified or third party- or EPA-accredited laboratory to verify minimal contamination in the laboratory.

At least three standards shall be used to develop the standard curve for SOC quantification and these three standards shall be extracted and analyzed (by GC or HPLC) on the same day as the samples.

During each Verification Test period, one treated water sample shall be analyzed by scanning for the presence and concentration of potential by-products of SOC disinfection by oxidation. Gas chromatography followed by mass spectrometry can be used to identify many of the organic by-products formed during oxidation disinfection. The spectra obtained by this analysis can be matched to a compound library in a computer database to identify the various by-products. This analysis shall be performed by a state-certified or third party- or EPA-accredited analytical laboratory. The scan should be targeted toward the SOC of interest, and the potential by-products associated with oxidation of that SOC.

Spiked samples shall be analyzed once, at the beginning of each Verification Test Run. The laboratory shall spike a feed water sample with a known quantity of the SOC(s) of interest and analyze this spiked sample. SOC analysis of the spiked sample will indicate if there are any interferences present in the feed water. The broad scan can be a

performance-based scan (i.e., the scan is not used for compliance, and therefore undergoes less rigorous QA/QC and is less expensive than a compliance based scan analysis.)

#### **14.6 Trip Control**

For tests utilizing spiked SOC<sub>s</sub>, a replicate or subsample of the spiking solution shall accompany the actual spiking solution from the analytical laboratory. This replicate sample shall undergo all of the processes used on the actual solution including dose preparation, shipping, preparation for spiking, and return to the laboratory for analysis. The trip control samples should show minimal loss of SOC<sub>s</sub>. Significant decreases in the SOC concentration of the trip control sample indicates that some step in handling the solution contributed to the reduction in the SOC concentration. The seeding tests must be repeated when significant loss of SOC<sub>s</sub> in the trip control sample is observed.

### **15.0 TASK 8: COST EVALUATION**

This Plan includes the assessment of costs of verification with the benefits of testing NF membrane processes over a wide range of operating conditions. Therefore, this Plan requires that one set of operating conditions be tested over a 60-day testing period. The equipment Verification Tests will provide information relative to systems, which provide desired results and the cost, associated with the systems. Design parameters are summarized in Table 15.1. These parameters will be used with the equipment Verification Test costs to prepare cost comparisons for Verification Testing purposes.

Capital and operation and maintenance (O & M) costs realized in the equipment Verification Test may be utilized for calculating cost estimates. O & M costs for each system will be determined during the equipment Verification Tests. The equipment costs will vary based on the cost of membrane equipment. The O & M costs that will be recorded and compared during the Verification Test include:

- Labor;
- Electricity;
- Chemical Dosage, and
- Equipment Replacement Frequency.

The capital and O & M costs will vary based on geographic location.



**Table 15.1: Design Parameters for Cost Analysis**

<b>Design Parameter</b>	<b>Specific Utility Values</b>
Raw water feed rate(mgd)	
Total required plant production rate(mgd)	
By-pass flow rate (mgd)	
Membrane flow rate (mgd)	
High/Low plant feedwater temperature (°C)	
Average Flux (gsfd/psi)	
Maximum Flux (gsfd/psi)	
Average cleaning frequency (days)	
High/Low feed TDS (mg/L)	

O & M costs should be provided for each membrane process that is tested. In order to receive the full benefit of the equipment Verification Test Programs, these costs should be considered along with quality of system operations. Other cost considerations may be added to the cost tables presented in this section as is needed prior to the start-up of the Verification Tests. A summary of O & M costs are outlined in Table 15.2.

**Table 15.2: Operations and Maintenance Cost**

Cost Parameter	Specific Values	
Labor rate + fringe (\$/personnel-hour)		
Labor overhead factor (% of labor)		
Number of O&M personnel hours per week		
Electric rate (\$/kWh)		
Membrane replacement frequency (%/year)		
Chemical Dosage (per week)		
O&M cost (\$/Kgal)		
	Dose	Bulk Chemical Cost
Chlorine (Disinfectant)		
Sulfuric acid (Pretreatment)		
Alum (Pretreatment)		
Hydrochloric acid (Pretreatment)		
Scale inhibitor <sup>2</sup> (Pretreatment)		
Caustic (Post-treatment)		
Sodium hydroxide (Membrane cleaning)		
Phosphoric acid (Membrane cleaning)		

<sup>1</sup>Information for cleaning chemicals and pretreatment chemicals (such as alum) should also be provided in this table. For cleaning agents, the concentration of the cleaning solution used to clean the membranes should be reported as the chemical dosed.

<sup>2</sup>Report the product name and manufacturer of the specific scale inhibitor used.

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## APPENDIX A - SOC HEALTH EFFECTS INFORMATION

**TABLE A.1: Regulated SOCs under Phase II of the SDWA**

PARAMETER	MCLG (mg/L)	MCL (mg/L)	Sources of Drinking Water Contamination	Potential Health Effects
2,4,5-TP (Silvex)	0.05	0.05	Herbicide on crops, right-of-ways, golf courses; canceled in 1982	Liver and kidney damage
2,4-D (Formula 40, Weedar 64)	0.07	0.07	Runoff from herbicide on wheat, corn, range lands, lawns	Liver and kidney damage
Acrylamide	Zero	TT	Polymers used in sewage and wastewater treatment	Cancer, nervous system effects
Alachlor (Lasso)	Zero	0.002	Runoff from herbicide on corn, soybeans, other crops	Cancer
Aldicarb	0.007	0.007	Insecticide on cotton, potatoes, other crops; widely restricted	Nervous system effects
Aldicarb sulfone	0.007	0.007	Biodegradation of Aldicarb	Nervous system effects
Aldicarb sulfoxide	0.007	0.007	Biodegradation of Aldicarb	Nervous system effects
Atrazine	0.003	0.003	Runoff from use as herbicide on corn and non-crop land	Mammary gland tumors
Carbofuran (Furdan 4F)	0.04	0.04	Soil fumigant on corn and cotton; restricted in some areas	Nervous, reproductivity effects
Chlordane	Zero	0.002	Leaching from soil treatment for termites	Cancer
Dibromochloropropane (DBCP, Nemaflume))	Zero	0.0002	Soil fumigant on soybeans, cotton, pineapple, orchards	Cancer
Ethyl benzene	0.7	0.7	Gasoline, insecticides, chemical manufacturing wastes	Liver, kidney, nervous system effects
Ethylene dibromide (EDB, Bromofume)	Zero	0.00005	Leaded gas additives, leaching of soil fumigant	Cancer
Heptachlor (H-34, Heptox)	Zero	0.0004	Leaching of insecticide for termites, very few crops	Cancer
Heptachlor epoxide	Zero	0.0002	Biodegradation of heptachlor	Cancer
Lindane	0.0002	0.0002	Insecticides for cattle, lumber, gardens; restricted in 1983	Liver, kidney, nervous system, immune system and circulatory system effects
Methoxychlor (DMDT, Marlate)	0.04	0.04	Insecticides for fruits, vegetables, alfalfa, livestock, pets	Growth, liver, kidney, and nervous system effects
Pentachlorophenol	Zero	0.001	Wood preservatives, herbicides, cooling tower wastes	Cancer, liver and kidney effects
Polychlorinated biphenyls (PCBs, Aroclor)	Zero	0.0005	Coolant oils from electrical transformers, plasticizers	Cancer
Toxaphene	Zero	0.003	Insecticide on cattle, cotton soybeans; canceled in 1982	Cancer

**TABLE A.2: Regulated SOC's under Phase V of the SDWA**

<b>PARAMETER</b>	<b>MCLG (mg/L)</b>	<b>MCL (mg/L)</b>	<b>Sources of Drinking Water Contamination</b>	<b>Potential Health Effects</b>
Adipate (diethylhexyl)	0.4	0.4	Synthetic rubber, food packaging, cosmetics	Decreased body weight
Dalapon	0.2	0.2	Herbicides on orchards, beans, coffee, lawns, roads, railways	Liver, kidney effects
Dinoseb	0.007	0.007	Runoff of herbicide from crop and non-crop allocations	Thyroid, reproductive organ damage
Dioxin	Zero	$3 \times 10^{-8}$	Chemical production by-product, impurity in herbicides	Cancer
Diquat	0.02	0.02	Runoff of herbicides on land and aquatic weeds	Liver, kidney, eye effects
Endothall	0.1	0.1	Herbicide on crops and land and aquatic weeds; rapidly degraded	Liver, kidney, gastrointestinal effects
Endrin	0.002	0.002	Pesticides on insects, rodents, birds; restricted since 1980	Liver, kidney, heart damage
Glyphosate	0.7	0.7	Herbicide on grasses, weeds, brush	Liver, kidney damage
Hexachlorobenzene	Zero	0.001	Pesticide production waste by-product	Cancer
Hexachlorocyclopentadiene	0.05	0.05	Pesticide production intermediate	Kidney, stomach damage
Oxamyl (Vydate)	0.2	0.2	Insecticide on apples, potatoes, tomatoes	Kidney damage
Phthalate	Zero	0.006	PVC and other plastics	Cancer
Phenanthrene (PAH)	Zero	0.0002	Coal tar coatings, burning organic matter, volcanoes, fossil fuels	Cancer
Picloram	0.5	0.5	Herbicide on broadleaf and woody plants	Kidney, liver damage
Simazine	0.004	0.004	herbicide on grass sod, some crops, aquatic algae	Cancer

## APPENDIX B – PROPOSED SOCS FOR REGULATION

<b>TABLE B.1: Proposed SOCs for Regulation</b>						
<b>Parameters</b>	<b>Regulatory Status.</b>	<b>MCLG (mg/L)</b>	<b>MCL (mg/L)</b>	<b>Status HA</b>	<b>RID (mg/kg/day)</b>	<b>DWEL (mg/L)</b>
Acetochlor	---	---	---	---	---	---
Acifluorfen	Tentative	zero	---	Final	0.013	0.4
Acrylonitrile	Tentative	zero	---	Draft	---	---
Aldrin	---	---	---	Draft	0.00003	0.001
Bromobenzene	Listed	---	---	Draft	---	---
Bromomethane	Tentative	---	---	Final	0.001	0.05
Cyanazine	Tentative	0.001	---	Draft	0.002	0.07
Diazinon	---	---	---	Final	0.00009	0.003
Dicamba	Listed	---	---	Final	0.03	1
Dichloroethane (1,1)	---	---	---	---	---	---
Dichloropropane (1,3-)	Listed	---	---	Draft	---	---
Dichloropropane (2,2-)	Listed	---	---	Draft	---	---
Dichloropropene (1,1-)	Listed	---	---	Draft	---	---
Dichloropropene (1,3-)	Tentative	zero	---	Final	0.0003	0.01
Diieldrin	---	---	---	Final	0.00005	0.002
Dinitrophenol (2,4)	---	---	---	---	---	---
Dinitrotoluene (2,4-)	Listed	---	---	Final	0.002	0.1
Dinitrotoluene (2,6-)	Listed	---	---	Final	0.001	0.04
Diphenylhydrazine (1,2)	---	---	---	---	---	---
Disulfoton	---	---	---	Final	0.00004	0.001
Diuron	---	---	---	Final	0.002	0.07
Fonofos	---	---	---	Final	0.002	0.07
Hexachlorobutadiene	Tentative	0.001	---	Final	0.002	0.07
Isopropyltoluene (p-)	---	---	---	---	---	---
Linuron	---	---	---	---	---	---
Methomyl	Listed	---	---	Final	0.025	0.9
Methyl Bromide	---	---	---	---	---	---
Methyl-Phenol (2-)	---	---	---	---	---	---
Methyl tert butyl ether (MTBE)	Listed	---	---	Draft	0.03	1
Metolachlor	Listed	---	---	Final	0.1	3.5
Metribuzin	Listed	---	---	Final	0.013	0.5
Molinate	---	---	---	---	---	---
Naphthalene	---	---	---	Final	0.004	0.1
Nitrobenzene	---	---	---	---	---	---
Organotins	---	---	---	---	---	---

<b>TABLE B.1: Proposed SOCs for Regulation (Cont.)</b>						
<b>Parameters</b>	<b>Regulatory Status.</b>	<b>MCLG (mg/L)</b>	<b>MCL (mg/L)</b>	<b>Status HA</b>	<b>RID (mg/kg/day)</b>	<b>DWEL (mg/L)</b>
Perchlorate	---	---	---	---	---	---
Prometon	Listed	---	---	Final	0.015	0.5
RDX	---	---	---	Final	0.003	0.1
Terbacil	---	---	---	Final	0.013	0.4
Terbufos	---	---	---	Final	0.00013	0.005
Tetrachoroethane (1,1,2,2-)	Listed	---	---	Draft	---	---
Triazine	---	---	---	---	---	---
Trichlorophenol	Listed	---	---	Draft	---	---
Trichloropropane (1,2,3-)	Listed	---	---	Final	0.006	0.2
Trifluralin	Listed	---	---	Final	0.0075	0.3
Trimethylbenzene (1,2,4-)	---	---	---	Draft	---	---

Sources:

1. US EPA Office of Water, "Drinking Water Regulations and Health Advisories", EPA-822-B-96-002, October 1996.
2. Federal Register, Volume 62, Number 193, October 6, 1997.

**CHAPTER 3**  
**EPA/NSF ETV**  
**EQUIPMENT VERIFICATION TESTING PLAN FOR SOC OXIDATION BY OZONE**  
**AND ADVANCED OXIDATION PROCESSES**

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## TABLE OF CONTENTS

	<u>Page</u>
<b>1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN .....</b>	<b>3-6</b>
<b>2.0 INTRODUCTION.....</b>	<b>3-6</b>
<b>3.0 GENERAL APPROACH.....</b>	<b>3-7</b>
<b>4.0 OVERVIEW OF TASKS.....</b>	<b>3-7</b>
4.1 Initial Operations: Overview .....	3-7
4.1.1 Task A: Characterization of Feed Water .....	3-7
4.1.2 Task B: Initial Test Runs.....	3-7
4.2 Verification Operations: Overview .....	3-8
4.2.1 Task 1: Verification Testing Runs and Routine Equipment Operation.....	3-8
4.2.2 Task 2: Feed Water and Finished Water Quality .....	3-8
4.2.3 Task 3: Documentation of Operating and Treatment Equipment Performance .....	3-8
4.2.4 Task 4: SOC Oxidation .....	3-8
4.2.5 Task 5: Data Management.....	3-9
4.2.6 Task 6: Quality Assurance/Quality Control (QA/QC) .....	3-9
<b>5.0 TESTING PERIODS .....</b>	<b>3-9</b>
<b>6.0 DEFINITION OF OPERATIONAL PARAMETERS .....</b>	<b>3-10</b>
6.1 Feed Gas or Ozone Production Concentration (% weight or g/m <sup>3</sup> NTP).....	3-10
6.2 Off Gas Concentration (% weight or g/m <sup>3</sup> NTP) .....	3-10
6.3 Applied Ozone Dosage (mg/L) .....	3-10
6.4 Transfer Efficiency (percent) .....	3-10
6.5 Transferred Ozone Dosage (mg/L) .....	3-11
6.6 Dissolved Ozone Concentration (mg/L) .....	3-11
6.7 Ozone Decay Rate (1/min).....	3-11
<b>7.0 TASK A: CHARACTERIZATION OF FEED WATER .....</b>	<b>3-11</b>
7.1 Introduction .....	3-11
7.2 Objectives.....	3-12
7.3 Work Plan .....	3-12
7.4 Analytical Schedule.....	3-12
7.5 Evaluation Criteria .....	3-13
<b>8.0 TASK B: INITIAL TEST RUNS .....</b>	<b>3-13</b>
8.1 Introduction .....	3-13
8.2 Objectives.....	3-13

## TABLE OF CONTENTS (continued)

	<b><u>Page</u></b>
8.3 Work Plan.....	3-13
8.4 Analytical Schedule.....	3-13
8.5 Evaluation Criteria .....	3-14
<b>9.0 TASK 1: VERIFICATION TESTING RUNS AND ROUTINE EQUIPMENT OPERATION .....</b>	<b>3-14</b>
9.1 Introduction .....	3-14
9.2 Experimental Objectives .....	3-14
9.3 Work Plan.....	3-14
9.3.1 Verification Testing Runs .....	3-14
9.3.2 Routine Equipment Operation.....	3-15
9.4 Schedule .....	3-15
9.5 Evaluation Criteria .....	3-15
<b>10.0 TASK 2: FEED WATER AND TREATED WATER QUALITY .....</b>	<b>3-15</b>
10.1 Introduction .....	3-15
10.2 Experimental Objectives .....	3-16
10.3 Work Plan.....	3-16
10.4 Analytical Schedule.....	3-16
10.5 Evaluation Criteria .....	3-17
<b>11.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE .....</b>	<b>3-17</b>
11.1 Introduction .....	3-17
11.2 Objectives.....	3-17
11.3 Work Plan.....	3-17
11.4 Schedule .....	3-18
11.5 Evaluation Criteria .....	3-18
<b>12.0 TASK 4: DOCUMENTATION OF EQUIPMENT PERFORMANCE: SOC OXIDATION .....</b>	<b>3-19</b>
12.1 Introduction .....	3-19
12.2 Experimental Objectives .....	3-19
12.3 Work Plan.....	3-19
12.3.1 Types of SOC's.....	3-19
12.3.2 Spiking Protocols .....	3-20
12.3.3 Test Operation and Sample Collection.....	3-20
12.3.4 Experimental Quality Control .....	3-21
12.3.5 Treatment of Effluent.....	3-21

## TABLE OF CONTENTS (continued)

	<b><u>Page</u></b>
12.4 Analytical Schedule.....	3-22
12.5 Evaluation Criteria .....	3-22
<b>13.0 TASK 5: DATA MANAGEMENT .....</b>	<b>3-22</b>
13.1 Introduction .....	3-22
13.2 Experimental Objectives .....	3-22
13.3 Work Plan.....	3-22
13.4 Statistical Analysis .....	3-23
<b>14.0 TASK 6: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC).....</b>	<b>3-24</b>
14.1 Introduction .....	3-24
14.2 Experimental Objectives .....	3-24
14.3 Work Plan.....	3-24
14.3.1 Daily QA/QC Verifications.....	3-24
14.3.2 QA/QC Verifications Performed Every Two Weeks .....	3-24
14.3.3 QA/QC Verifications Performed Every Testing Period.....	3-25
14.4 On-Site Analytical Methods.....	3-25
14.4.1 pH.....	3-25
14.4.2 Turbidity Analysis .....	3-25
14.4.2.1 Bench-top Turbidimeters.....	3-26
14.4.2.2 In-line Turbidimeters.....	3-26
14.4.3 Dissolved Ozone .....	3-26
14.4.4 Gas Phase Ozone.....	3-27
14.4.5 Hydrogen Peroxide.....	3-27
14.4.6 Temperature .....	3-28
14.4.7 Color.....	3-28
14.4.8 Dissolved Oxygen .....	3-28
14.5 Chemical and Biological Samples Shipped Off-Site for Analysis.....	3-29
14.5.1 Organic Samples .....	3-29
14.5.2 Algae .....	3-29
14.5.3 Inorganic Samples .....	3-29
14.5.4 SOC Analysis .....	3-29
14.6 Experimental QA/QC Samples .....	3-30
14.6.1 Process Control .....	3-30
14.6.2 Trip Control.....	3-31
<b>15.0 OPERATION AND MAINTENANCE .....</b>	<b>3-31</b>
15.1 Maintenance .....	3-31
15.2 Operation.....	3-32

## TABLE OF CONTENTS (continued)

	<u>Page</u>
<b>16.0 REFERENCES</b> .....	3-33

### TABLES

Table 1	Water Quality Sampling and Measurement Schedule.....	3-34
Table 2	Analytical Methods .....	3-37
Table 3	Package Treatment Plant Operating Data.....	3-39

## **1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN**

This document is the NSF Environmental Technology Verification (ETV) Plan for evaluation of water treatment equipment utilizing ozone for oxidation of man-made or synthetic organic chemicals (SOCs). This Testing Plan is to be used as a guide in the development of the Field Operations Document (FOD) for testing ozone equipment, within the structure provided by the NSF "Protocol for Equipment Verification Testing of Synthetic Organic Contamination Removal." This ETV plan is applicable only to treatment systems that rely on ozone to oxidize SOCs in water. Systems using ozone oxidation for reasons other than SOC oxidation (i.e., taste and odor control, disinfection) are not required to conduct the experiments outlined in this ETV plan. Systems may incorporate unique strategies for enhancing the effect of ozone on SOC concentrations, such as the use of ozone/advanced oxidation processes (ozone/AOPs) combining ozone with ultraviolet (UV) light or hydrogen peroxide. All ozone technologies, including ozone/AOPs, may be tested under this plan.

In order to participate in the equipment verification process for SOC oxidation by ozone or ozone/AOPs, the equipment Manufacturer and the designated Field Testing Organization shall use the procedures and methods described in this test plan, and in the "Protocol for Equipment Verification Testing of Synthetic Organic Contamination Removal" as guidelines for development of the FOD.

This ETV plan is applicable to the testing of water treatment equipment utilizing ozone or ozone/AOPs for SOC oxidation in drinking water. This plan is applicable to both surface water and groundwater supplies.

## **2.0 INTRODUCTION**

The organic compounds present in source waters are characterized as either: 1) naturally occurring (e.g., humic acid, fulvic acid); or 2) synthetic (e.g., pesticides, hydrocarbons, phenols, dyes, amines, solvents, and plasticizers, etc.). A complete listing of those synthetic organic compounds (SOCs) regulated by the USEPA is not presented in this document, but can be found in Pontius (1998). Other SOCs, which are not currently regulated by the USEPA, may be evaluated with this ETV plan. These unregulated SOCs, some of which are being considered for regulation in the near future, include metolachlor, MTBE, and triazines. A listing of SOCs likely to be regulated in the future can be found in the USEPA's "Drinking Water Regulations and Health Advisories," and the current Drinking Water Contaminant Candidate List, available from the Safe Drinking Water Hotline (1-800-426-4791).

Ozone is a powerful oxidant that is applied during water treatment for microbial inactivation as well as oxidation of organic compounds, metals, and taste and odor causing compounds. The use of ozone in potable water treatment in the United States has increased substantially in the last 20 years, due to its superior inactivation of microorganisms (i.e., cysts) relative to chlorine, chloramine, and chlorine dioxide and its ability to reduce the concentrations of certain organics in drinking water.

Ozone is applied to drinking water as a gas, which is generated on-site. The ozone gas is transferred into a dissolved state by either bubbling or injecting ozone gas into the process

stream. Ozone can be applied to untreated (raw) or treated (e.g., coagulated/settled or filtered) water. In this ETV plan, the oxidation of SOC's by ozone or ozone/AOPs will be evaluated. Ozone/AOPs, which typically combine ozonation with UV light or hydrogen peroxide, convert dissolved ozone to hydroxyl radicals. In many instances, ozone/AOPs can be more effective than ozone used by itself for oxidation of SOC's.

### **3.0 GENERAL APPROACH**

Testing of equipment covered by this ETV plan will be performed by an NSF-qualified Field Testing Organization (FTO) that is selected by the equipment Manufacturer. Water quality analytical work to be carried out as part of this ETV plan will be contracted with a state-certified or third party- or EPA-accredited qualified analytical laboratory.

### **4.0 OVERVIEW OF TASKS**

#### **4.1 Initial Operations: Overview**

The purpose of these tasks is to provide preliminary information which will facilitate final test design and data interpretation.

##### **4.1.1 Task A: Characterization of Feed Water**

The objective of this Initial Operations task is to obtain a chemical and physical characterization of the feed water for those systems using ozone or ozone/AOPs for SOC oxidation. Historical records of SOC concentrations in the feed water shall be reviewed to evaluate the use of ozone or ozone/AOPs at the site.

A thorough description of the watershed or aquifer and any pretreatment modules that provide the feed water should be prepared, to aid in interpretation of feed water characterization.

##### **4.1.2 Task B: Initial Test Runs**

During Initial Operations, the manufacturer may want to evaluate equipment operation and determine flow rates, hydraulic retention time, ozone dosage, optimum pH, sequencing or timing of UV light and/or hydrogen peroxide addition relative to ozonation, or other factors which provide effective treatment of feed water. This is a recommended Initial Operations task.

The FTO may also want to work with the analytical laboratory to perform blank or preliminary challenges and sampling routines to verify that sampling equipment can perform its required functions. This is also a recommended Initial Operations Task.

## **4.2 Verification Operations: Overview**

The objective of this task is to operate for a minimum of one test period the treatment equipment provided by the FTO and to assess its ability to meet stated water quality goals and any other performance characteristics specified by the Manufacturer. The equipment shall be operated to collect data on equipment performance and water quality for purposes of performance verification. The test period selected should represent the worst-case for concentrations of ozone demanding contaminants (e.g., iron, organics, hydrogen sulfide, pesticides, or turbidity) and for presence of synthetic organic contaminants.

### **4.2.1 Task 1: Verification Testing Runs and Routine Equipment Operation**

To characterize the technology in terms of efficiency and reliability, package plant water treatment equipment that includes ozone (or ozone/AOPs) shall be operated for Verification Testing purposes with the operational parameters based on the results of the Initial Operations testing.

### **4.2.2 Task 2: Feed Water and Finished Water Quality**

During each Verification Testing period, feed water and treated water samples shall be collected and analyzed for those parameters relevant to oxidation performance and affecting equipment performance, as outlined in Section 10, Table 1.

### **4.2.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance**

During each Verification Testing period, operating conditions and performance of water treatment equipment shall be documented. This includes ozone feed gas concentration, gas and liquid pressures, gas and liquid temperatures, gas and liquid flow rates, ozone off-gas concentration, applied and transferred ozone dosage, power usage for the ozone generator, ozone transfer equipment, ozone feed-gas and off-gas monitors (if part of the ozone system) and ozone destruct unit, as well as stability of the electrical power supply (surges, brown-outs, etc.).

If ozone (or an AOP) is used following pretreatment (e.g., coagulation/settling), then a complete description of the pretreatment process shall be provided. For AOP systems, the operating conditions and parameters associated with hydrogen peroxide or UV light equipment must also be documented.

### **4.2.4 Task 4: SOC Oxidation**

The objective of this task is to evaluate SOC oxidation during Verification Testing by measuring the SOC concentrations of interest in the feed water and in the treated water. If the SOC concentration naturally present in the feed water is not sufficiently high for testing, SOC spiking is needed. Another requirement of this task is to provide a gas chromatography/mass spectrometry scan of the organic by-products formed by ozonation of SOC.

#### **4.2.5 Task 5: Data Management**

The objective of this task is to establish an effective field protocol for data management at the field operations site and for data transmission between the FTO and the NSF for data obtained during the Verification Testing. Prior to the beginning of field testing, the database design must be developed by the FTO and reviewed and approved by NSF. This will ensure that the required data will be collected during the testing, and that it can be effectively transmitted to NSF for review.

#### **4.2.6 Task 6: Quality Assurance/Quality Control (QA/QC)**

An important aspect of Verification Testing is the protocol developed for quality assurance and quality control. The objective of this task is to assure accurate measurement of operating and water quality parameters during ozone equipment Verification Testing. Prior to the beginning of field testing, a QA/QC plan must be developed which addresses all aspects of the testing process. Each water quality parameter and operational parameter must have appropriate QA and QC measures in place and documented. For example, the protocol for ozone measurement using a spectrophotometer should describe how the instrument is calibrated, what adjustments are made, and provide a permanent record of all calibrations and maintenance for that instrument.

### **5.0 TESTING PERIODS**

The required tasks in the Verification Testing Plan (Tasks 1 through 6) are designed to be carried out during one or more testing periods, each of which shall provide at least 200 hours of ozone equipment operation. During this time, the performance and reliability of the equipment shall be documented.

Some systems may operate for less than 24 hours per day. Interruptions in ozone production are allowed but the reason for and duration of all interruptions shall be fully described in the Verification Testing report. Any testing conducted at intervals of less than 200 hours is considered a test *run*, whereas the entire 200 hours (either continuous or as the sum of individual test runs) of ozone equipment operation is considered the Verification Test *period*. If ozone production is interrupted during a verification test run, that test run shall be considered to have been concluded at the time of interruption of the ozone feed. After restart, all data collected are to be part of a new verification test run.



## 6.0 DEFINITION OF OPERATIONAL PARAMETERS

Definitions that apply to ozone and ozone/AOP processes are given below. Refer to Appendix A of *Ozone in Water Treatment, Application and Engineering*, by the American Water Works Association Research Foundation and Compagnie Générale des Eaux, Lewis Publishers, 1991 for a more detailed description of terms.

### 6.1 Feed Gas or Ozone Production Concentration (% weight or g/m<sup>3</sup> NTP)

The feed gas or ozone production concentration ( $Y_1$ ) is the ozone concentration (in gaseous form) being applied to the water being treated. It is expressed in units of g/m<sup>3</sup> normal temperature and pressure (NTP) or as percent by weight. The temperature and pressure values associated with NTP are 0 °C and one atmosphere (i.e., 14.696 psi, 760 mm Hg, or 101.325 kPa), respectively.

### 6.2 Off Gas Concentration (% weight or g/m<sup>3</sup> NTP)

The off gas concentration ( $Y_2$ ) is the ozone concentration (in gaseous form) of the gas which is being released (i.e., off gas) from the water being treated. This off gas contains ozone which was not transferred into a dissolved form during treatment. It is expressed in units of g/m<sup>3</sup> NTP or as percent by weight.

### 6.3 Applied Ozone Dosage (mg/L)

The amount of ozone added to the water being treated is the applied ozone dosage. The equation for calculating the applied ozone dosage is as follows:

$$D = P/(8.34 \cdot L)$$

where: D = applied ozone dosage (mg/L)

P = ozone production (lb/day)

L = water flow rate (MGD, million U.S. gallons per day )

### 6.4 Transfer Efficiency (percent)

The transfer efficiency is defined as the percentage of ozone that becomes dissolved into the water being treated. The equation for calculating the transfer efficiency is as follows:

$$TE = [(Y_1 - Y_2)/Y_1] \cdot 100$$

where: TE = transfer efficiency (percent)

$Y_1$  = ozone production concentration (g/m<sup>3</sup> NTP or percent by weight)

$Y_2$  = off gas ozone concentration (g/m<sup>3</sup> NTP or percent by weight)

This calculation assumes that the flow of the feed gas is equal to the flow of the off gas. The transfer efficiency calculation can be refined by measuring both gas flow rates or by monitoring the dissolved gas concentration in the liquid phase if the Manufacturer and their FTO desire.

## 6.5 Transferred Ozone Dosage (mg/L)

The transferred ozone dosage is the concentration of ozone that becomes dissolved into the water being treated. The equation for calculating the transferred ozone dosage is as follows:

$$T = (D * TE)/100$$

where: T = transferred ozone dosage (mg/L)  
D = applied ozone dosage (mg/L)  
TE = transfer efficiency (percent, i.e., 95.0 and not 0.95)

## 6.6 Dissolved Ozone Concentration (mg/L)

The concentration of ozone in solution is the dissolved ozone concentration. It is measured using an indigo bleaching technique (e.g., HACH AccuVac or *Standard Method* 4500-O<sub>3</sub> B) or by inserting a dissolved ozone probe into the process stream (e.g. Orbisphere, Orbisphere Laboratories, Emerson, NJ).

## 6.7 Ozone Decay Rate (1/min)

After the initial ozone demand has been satisfied, the ozone decay rate is assumed to follow pseudo first-order kinetics. Monitoring the decay rate will provide an indication of the level of ozone demanding substances present in the feed water and the environmental conditions affecting oxidation (e.g., pH and temperature). To calculate the decay rate, the initial ozone concentration (C<sub>o</sub>) at time zero and the ozone concentration (C) after time, t, must be known. The equation for calculating the decay rate (k) is as follows:

$$C = C_o e^{-kt}$$

Where: C = ozone concentration at time t (mg/L)  
C<sub>o</sub> = ozone concentration at time zero (mg/L)  
t = contact time (minutes)  
k = decay coefficient (1/minute)

If possible, the ozone residual should be measured after several contact times in the reactor. The best fit line of ln(C/C<sub>o</sub>) versus t can be used to obtain the decay coefficient, k. If the plot does not fit a straight line, the assumption of pseudo-first order kinetics is not valid.

## 7.0 TASK A: CHARACTERIZATION OF FEED WATER

### 7.1 Introduction

This recommended Initial Operations task is performed to determine if the chemical, biological, and physical characteristics of the feed water are appropriate for the water treatment equipment to be tested.

Initial Operations (Tasks A and B) are not mandatory but they are recommended as an aid to successful completion of Verification Testing. If the verification entity conducts a site visit for QA purposes, then Task B would need to be performed.

## **7.2 Objectives**

The objective of this task is to obtain a complete chemical and physical characterization of the source water, or the feed water after pre-treatment, that will be entering the treatment system being tested.

## **7.3 Work Plan**

During this Initial Operations task, the following water quality characteristics of the feed water to the ozone system should be measured and recorded for both ground and surface waters: ozone demand, turbidity, temperature, pH, alkalinity, calcium, total hardness, total sulfides, total organic carbon, dissolved organic carbon, ultraviolet absorbance (at 254 nm), color, bromide, iron, and manganese. Data on SOC's in the feed water (source water) should be obtained from existing data bases or by analysis of water samples, so a determination about the need for SOC spiking can be made.

Sufficient information shall be obtained to illustrate the variations expected to occur in these parameters that will be measured during the Verification Testing for a typical annual cycle for the water source. This information will be compiled and shared with NSF so NSF and the FTO can determine the adequacy of the data for use as the basis to make decisions on the testing schedule.

A brief description of the watershed or aquifer source shall be provided, to aid in interpretation of feed water characterization. The watershed description should include a statement of the approximate size of the watershed, a description of the topography (i.e., flat, gently rolling, hilly, mountainous) and a description of the kinds of human activity that take place (i.e., mining, manufacturing, cities or towns, farming, wastewater treatment plants) with special attention to potential sources of pollution that might influence feed water quality. The nature of the water source, such as stream, river, lake or man-made reservoir, should be described as well. Aquifer description should include (if available) the above characterization relative to the recharge zone, a description of the hydrogeology of the water bearing stratum(a), well boring data, and any Microscopic Particulate Analysis data indicating whether the groundwater is under the influence of surface waters.

Any pretreatment, including oxidation, coagulation or pH adjustment, of the water upstream of the ozone equipment shall be completely documented and characterized. Any coagulant or other chemical additions shall be identified and the chemical form and dosage shall be fully described.

## **7.4 Analytical Schedule**

There is no recommended analytical schedule for characterization of the feed water. Any existing water quality data should be reviewed to assess the character of the feed or source water as well as the range of water quality that can be expected during each season. Water quality sampling can be performed if there are data gaps in the existing information.

## **7.5 Evaluation Criteria**

Feed water quality will be evaluated in the context of the Manufacturer's statement of the equipment performance capabilities but should not be beyond the range of water quality suitable for treatment for the equipment in question. The device shall be tested using water of the quality for which the equipment was designed.

## **8.0 TASK B: INITIAL TEST RUNS**

### **8.1 Introduction**

During the Initial Operations, a Manufacturer and their FTO may choose to evaluate equipment operations and determine flow rates, hydraulic residence time, ozone production, power supply requirements, or other factors applicable to the technology and related to effective treatment of the feed water, including the weight ratios of hydrogen peroxide to ozone dosages and/or the ratios of UV to ozone dosages. The Manufacturer may also choose to work with the FTO and the analytical laboratory to perform blank or preliminary challenges (if necessary) and sampling routines to verify that sampling equipment can perform the required functions under normal operating conditions. This information may also indicate operating conditions under which the Manufacturer's stated performance capabilities are not met. This is a recommended Initial Operations task. An NSF field audit of equipment operations and sampling and field analysis procedures may be carried out during the initial test runs, and if this occurs, the Initial Operations task must be performed.

### **8.2 Objectives**

The objective of these test runs is to bracket the proper operating parameters for treatment of feed water during Verification Testing. The ability of ozone or ozone/AOP systems to effectively oxidize SOC<sub>2</sub>s and reduce their concentrations will vary depending on the quality of the feed water being treated and the season. Therefore, conducting initial test runs is strongly recommended.

### **8.3 Work Plan**

Because Initial Operations test runs are not a requirement of this ETV plan, the Manufacturer and FTO can decide the duration of Initial Operations. Enough time should be available to establish optimal operating conditions and to ensure that the system will be able to meet any performance objectives.

### **8.4 Analytical Schedule**

Because these Initial Operations are being conducted to define future operating conditions for Verification Testing, a strictly defined schedule for sampling and analysis does not need to be followed. Adhering to the schedule for sampling and analysis to be followed during Verification Testing is recommended, however, so the operator can gain familiarity with the time

requirements that will be applicable during Verification Testing. Also, during the Initial Operations phase, the verification organization may conduct an initial on-site audit of field operations, sampling activities, and on-site analyses. The sampling and analysis schedule that is to be used during Verification Testing shall be followed during the on-site audit.

## **8.5 Evaluation Criteria**

The Manufacturer and the FTO should evaluate the data produced during the Initial Operations to determine if the water treatment equipment performed in a manner that will meet or exceed the statement of performance capabilities. If performance is not as good as in the statement of performance capabilities, the FTO may conduct additional Initial Operations or cancel the remainder of the testing program.

## **9.0 TASK 1: VERIFICATION TESTING RUNS AND ROUTINE EQUIPMENT OPERATION**

### **9.1 Introduction**

Package plant water treatment equipment that includes ozone or ozone/AOPs shall be operated for Verification Testing purposes with operational parameters based on the manufacturer's statement of performance capabilities.

### **9.2 Experimental Objectives**

The objective of this task is to operate the ozone or ozone/AOP equipment and characterize the effectiveness and reliability of the equipment.

### **9.3 Work Plan**

#### **9.3.1 Verification Testing Runs**

The Verification Testing Runs in this task consists of an evaluation of the treatment system, using the most successful treatment parameters defined during Initial Operations. Performance and reliability of the equipment shall be tested during one or more Verification Testing periods consisting of at least 200 hours of ozone production at the test site.

Verification Testing should be conducted at times when worst-case seasonal water quality conditions exist, including peak concentrations of SOC's or of hydroxyl free radical-demanding contaminants or ozone-demanding contaminants. During each of these testing periods, Tasks 1 through 6 shall be conducted simultaneously.

Factors that can influence SOC oxidation include:

- the presence of ozone demanding substances that may be present in the form of particulate matter, dissolved organic matter, or dissolved inorganic matter; often occurring in the spring, or during reservoir or lake turn-over events, or also encountered in rivers carrying a high sediment load or in surface waters during periods of high runoff resulting from heavy rains or snow melt. Algae also exert an ozone demand as do iron, manganese, and cyanide. The presence of ozone demanding substances will affect the ability of ozone to effectively oxidize SOC's and will react with hydroxyl free radicals needed to destroy the slower-to-oxidize SOC's.
- pH and alkalinity, which can vary seasonally, will affect the decay rate of ozone in natural waters, and may affect the amount of SOC oxidation achieved by the system.
- temperature.

### **9.3.2 Routine Equipment Operation**

If the package water treatment equipment is being used for production of potable water during the time intervals between verification runs, routine operation of the equipment will occur. In this situation, the operating and water quality data collected and furnished to the Safe Drinking Water Act (SDWA) primacy agency shall be supplied to the NSF-qualified FTO for use in evaluating conditions during verification testing.

For equipment that is being used to treat water for distribution to customers, it is assumed that the State has already issued a permit (if one is necessary) for installation and operation. If ETV is being conducted to establish the SOC oxidation capabilities of the existing equipment, permission by the State may be required if the system were taken off-line for verification testing.

## **9.4 Schedule**

During Verification Testing, water treatment equipment shall be operated for a minimum of 200 hours. The reason for and duration of any interruptions in ozone production during Verification Testing shall be fully documented.

## **9.5 Evaluation Criteria**

The goal of this task is to operate the equipment for 200 hours during Verification Testing. Data shall be provided to substantiate that 200 hours of operation have been completed.

# **10.0 TASK 2: FEED WATER AND TREATED WATER QUALITY**

## **10.1 Introduction**

Water quality data shall be collected during Verification Testing for the feed water and treated water as shown in Table 1. The Field Test Organization, on behalf of the equipment Manufacturer, shall assure the sampling or measuring of the water quality parameters in Table 1.

The FTO may use local personnel to assist in collection of samples or measurement of test parameters, but is responsible for their training to assure proper techniques are used at all times.

## **10.2 Experimental Objectives**

The objective of this task is to identify the presence and concentration of water quality characteristics that might affect the ability of ozone to oxidize SOC<sub>s</sub>. This task will also provide data to ensure that the use of ozone does not increase the risk of violating any existing or future SDWA regulations (e.g., THMs, bromate).

## **10.3 Work Plan**

The Manufacturer or FTO will be responsible for establishing the testing operating parameters, on the basis of the Initial Operations testing. Many of the water quality parameters described in this task will be measured on-site by the NSF-qualified FTO or by local community personnel properly trained by the FTO. Analysis of the remaining water quality parameters will be performed by a state-certified or third party- or EPA-accredited analytical laboratory. The methods to be used for measurements of water quality parameters in the field are listed in the Analytical Methods section in Table 2. The analytical methods utilized in this study for on-site monitoring of feed water and treated water qualities are described in Task 6, Quality Assurance/Quality Control (QA/QC). Where appropriate, the *Standard Methods* reference numbers for water quality parameters are provided for both the field and laboratory analytical procedures. EPA Methods for analysis of the parameters listed in Table 2 also may be used.

Samples of the feed water shall be collected and analyzed for background SOC concentrations. Feed water shall also be sent to the state-certified or third party- or EPA- accredited laboratory to conduct spiking QA/QC analysis (see Task 6). The approved analytical methods for SOC<sub>s</sub> vary, depending on the SOC<sub>s</sub> of interest. A state-certified or third party- or EPA-accredited laboratory should be using an approved EPA or *Standard Method* for SOC analysis. Peer-reviewed and proposed methods for SOC determination are also allowable if approved EPA or *Standard Methods* are not available. The preservatives needed for sample collection also vary for different SOC<sub>s</sub> and the state-certified or third party- or EPA-accredited should fully document sampling requirements for the FTO.

Any disinfectant added upstream of the ozone addition point will affect the ozone demand; therefore, an agreement between NSF, the manufacturer, and the FTO must be made to determine whether or not to allow pre-disinfection prior to ozonation during the Verification Testing Period. If a pre-disinfectant is used, testing shall be conducted to verify that no disinfectant residual exists at the influent of the ozone contactor, or if a disinfectant residual does exist, a quenching solution (e.g., sodium bisulfite or hydrogen peroxide) shall be used. The latter option (quenching) is less desirable because the concentration of the quenching agent will have to be carefully monitored during testing to minimize over-feeding of the quenching agent (which would result in an ozone demand).

## **10.4 Analytical Schedule**

Water quality data shall be collected at the intervals specified in Table 1. Additional sampling and data collection may be performed at the discretion of the Manufacturer and their designated

FTO. Sample collection protocol shall be defined by the FTO in the FOD. Algae sampling is not required for systems using groundwater sources.

For water quality samples that will be shipped to a state-certified or third party- or EPA-accredited laboratory for analysis, the samples shall be collected in appropriate containers (containing preservatives as needed) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the laboratory. Original field sheets and chain-of-custody forms shall accompany all samples shipped to the laboratory. Copies of field sheets and chain-of custody forms for all samples shall be provided to NSF.

## **10.5 Evaluation Criteria**

The performance of the ozone or ozone/AOP equipment will be compared to the Manufacturer's statement of performance for the equipment being tested. Evaluation of water quality in this task is related to meeting the MCLs for SOC's of Phase II and Phase V (listed in Pontius, 1998) as well as for other SOC's which may be regulated in the future (listed in USEPA's October 1996 Drinking Water Regulations and Health Advisories, at [www.epa.gov](http://www.epa.gov)). The ability of the ozone or AOP to meet other existing or future SDWA regulations (e.g., THMs, bromate) will also be evaluated.

## **11.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE**

### **11.1 Introduction**

Throughout the Verification Testing period, operating conditions shall be documented. This shall include descriptions of pretreatment chemistry and filtration performance for the package plant processes, if used, and their operating conditions. The performance of the ozone equipment (including ozone generator(s), air preparation system(s), off-gas destruct unit(s), injection equipment, ozone monitor(s), and contactor(s)) as well as UV light and hydrogen peroxide equipment shall be documented. The total volume of water treated and the total power usage for all equipment associated with the ozone or ozone/AOP system shall also be recorded.

### **11.2 Objectives**

The objective of this task is to accurately and fully document the operating conditions during treatment, and the performance of the equipment. This task is intended to collect data that describe operation of the equipment and information that can be used to develop cost estimates for operation of the equipment.

### **11.3 Work Plan**

During Verification Testing, treatment equipment operating parameters for both pretreatment and ozonation shall be monitored and recorded on a routine basis by the NSF-qualified FTO or by local community personnel properly trained by the FTO.



Table 3 outlines some of the operating parameters that shall be monitored throughout Verification Testing. Operating parameters, in addition to those listed in Table 3, may be needed to adequately assess the operating conditions of the ozone or ozone/AOP equipment. These additional parameters shall be identified by the Manufacturer and the FTO and agreed upon by the Manufacturer and NSF.

Examples of operational parameters which shall be monitored are:

- water flow rates
- gas flow rates
- water pressures
- gas pressures
- water temperatures
- gas temperatures
- ozone operating voltage
- ozone production power consumption
- air preparation power consumption or other consumables for air preparation
- oxygen feed rate (if applicable) and other pertinent operation information
- performance of oxygen generation or oxygen feed equipment
- ozone electrical frequency, if variable
- amperage of ozone equipment
- weight ratio of hydrogen peroxide (if used) to ozone

On a daily basis, the operator shall note and record whether any visual effects of ozonation are apparent in the treated water or on piping or vessels that convey or hold treated water. This may include surface scum, precipitation of metals, color changes, etc. At the end of the test period if an ozone contact chamber is provided with the equipment and if it is accessible, the contact chamber shall be inspected for deposits of scum, precipitation of metals, or color changes, and this information shall be noted in the Verification Testing report.

#### **11.4 Schedule**

Table 3 presents the schedule and recording data required for ozone and AOP systems. The length of time (hours) of operation (during Verification Testing) shall be recorded for all of the ozone and AOP equipment.

#### **11.5 Evaluation Criteria**

Where applicable, the data developed from this task will be compared to statements of performance capabilities. If no relevant statement of performance capability exists, results of operating and performance data will be tabulated for inclusion in the Verification Report.

## **12.0 TASK 4: DOCUMENTATION OF EQUIPMENT PERFORMANCE: SOC OXIDATION**

### **12.1 Introduction**

The ability of ozone and AOP equipment to oxidize SOC(s) can be assessed by measuring the initial and final SOC concentrations and computing the change (see Chapter 1 of the Protocol for Equipment Verification Testing of Synthetic Organic Contamination Removal).

### **12.2 Experimental Objectives**

The objective of this task is to determine the effectiveness of ozone or ozone/AOP equipment for SOC oxidation at small system packaged plants.

### **12.3 Work Plan**

The FTO shall conduct water quality sampling and calculate the reduction in SOC concentration(s) resulting from ozone or AOP treatment. Task 4 shall be conducted during the Verification Testing runs conducted in Task 1, 2, and 3.

The background or naturally occurring concentration of the SOC(s) of interest shall be determined during either Task A or Task 2 so that the background concentration of SOC(s) in the feed water is known prior to conducting Verification Testing. If the background SOC concentration is too low to adequately show or calculate a percentage removal, spiking of SOC(s) during the 200 hours of Verification Testing will be necessary.

Multiple SOC(s) can be simultaneously evaluated during Verification Testing; however, ozone or AOPs may preferentially react with naturally occurring organics or other SOC(s) present in solution, thereby reducing its ability to oxidize the SOC(s) of interest. Thus, it is possible that the desired outcome of Verification Testing may not occur during some multiple SOC evaluations.

If the ozone or AOP equipment is already being used at a site and has been approved by the State (if necessary), a manufacturer may want to verify its performance with Verification Testing. This can be accomplished by conducting the tests at the location if naturally occurring or background SOC concentrations are high enough for accurately and precisely calculating reductions. This would not compromise the water quality in any way. However, if SOC(s) must be spiked for testing, this poses a potential threat to the water quality. In this case, identical equipment would have to be brought on site and spiked SOC studies would have to be conducted with this additional equipment. The effluent of this spiked SOC testing would be treated as described in Section 12.3.5.

#### **12.3.1 Types of SOC(s)**

The SOC(s) covered by this ETV plan include Phase II and Phase V SOC(s), as well as those being studied by the USEPA (see the USEPA's October, 1996 Drinking Water Regulations and Health Advisories; [www.epa.gov](http://www.epa.gov))

This ETV plan is not designed to guide Verification Testing for volatile organic compounds (VOCs). Examples of VOCs include benzene and vinyl chloride, and a list of regulated VOCs (i.e., Phase I) can be found in Pontius (1998).

Oxidation of SOC(s) by ozone or AOPs can form by-products. The presence and concentration of these by-products is of interest because some of the by-products are considered as potential health concerns as a result of long-term exposure. Therefore, it is necessary that one treated water sample be collected during each Verification Test period, and this sample will be analyzed for the presence and concentration of by-products. This can be accomplished by conducting a scan of semi-volatile organic by-products by using gas chromatography/mass spectrometry by an state-certified or third party- or EPA-accredited analytical laboratory that has scanning and compound library matching capabilities. Some of the common by-products include: aldehydes, ketones, and for atrazine, deethylatrazine and deisopropylatrazine.

### **12.3.2 Spiking Protocols**

Spiking of SOC(s) shall be used in concentrations sufficient to permit the highest level of stress for the Manufacturer's equipment. Some guidelines for spiking include:

- SOC spiking shall begin at start-up of the treatment equipment and shall continue for the 200 hours of Verification Testing.
- The SOC(s) feed solution shall be prepared by diluting the SOC into dilution water that is distilled or deionized and oxidant demand-free.
- The container used for storing the feed SOC solutions shall be chemically inert (i.e., not reactive or adsorbable with the SOC(s) of interest).
- The feed solution shall be gently and continuously mixed throughout the Verification Test Run.
- The SOC spiked solution shall be fed using an adjustable rate chemical feed pump.
- Use of an in-line static mixer to mix this solution into the feedwater is recommended.
- SOC samples shall be collected in sample bottles prepared (i.e., preservatives added, if necessary) by the analytical laboratory performing the analysis.
- Multiple SOC(s) can be contained in the same stock feed container (i.e., having only one feed solution).
- The concentration of SOC(s) applied to the feed water shall be agreed upon by the Manufacturer, NSF, and the FTO.

### **12.3.3 Test Operation and Sample Collection**

If spiking is necessary, the SOC(s) of interest shall be continuously applied to the feed water during the 200 hours of Verification Testing. If an ozone or ozone/AOP system is temporarily shut down, then the spiking solution feed equipment should also be shut down and then started again when the ozone or ozone/AOP system is started again.

During the Verification Testing period, SOC samples of the feed water and treated water shall be collected once per 25 hours of operation. If the ozone or ozone/AOP system is not operating continuously, then the SOC samples shall be collected after the mid-point of the run in which the equipment is being operated. For example, if the ozone system is operated in 8 hour shifts, the SOC samples shall be collected after the fourth hour of operation.

During sample collection, minimal sample agitation and exposure to the atmosphere shall occur. An overflowing technique for filling samples bottles is recommended. A piece of Tygon tubing attached to the sample port can be placed such that the unattached end of the tubing rests at the bottom of the sampling container. As the sample fills the bottle, the end of the tubing remains at the bottom of the container. Once the sampling container is overflowing, the tubing can slowly be removed from the container. The lid should be placed on the container immediately after the sample tube is removed from the sample container.

Since some SOC samples require the use of a preservative in the sampling container, the overflowing technique is not applicable to all SOC(s). If this is the case, the Tygon tubing is still recommended (to minimize sample agitation during collection); however, the tubing should be removed prior to the point at which the sample would overflow the container.

Samples shall be delivered to a state-certified or third party- or EPA-accredited analytical laboratory for analysis using approved EPA or *Standard Methods* for measuring the SOC concentrations of interest.

#### **12.3.4 Experimental Quality Control**

Duplicates of the feed and treated water samples shall be collected for at least two of the sampling events during a Verification Test Run. A process control and trip control sample shall also be collected as part of Task 6.

The experimental quality control shall be verified by checking the flow rate of the spiked solution once per day. To ensure the proper feed rate of the spiked SOC solution to the ozone or AOP system, use a stopwatch to measure the time required to collect a specified volume of the feed solution from the feed system. This requires that the feed line to the contactor be temporarily disconnected so that the pumping rate of the stock SOC solution can be measured. Typically, a graduated cylinder is used to collect the pumped SOC sample and the size of the graduated cylinder is such that the length of collection time exceeds 10 seconds.

#### **12.3.5 Treatment of Effluent**

Treated water resulting from SOC spiking experiments using ozone or ozone/AOP equipment shall not be distributed to the public. The treated water might have to be passed through a granular activated carbon (GAC) filter for removal of residual SOC's during the 200 hours of Verification testing. The size of the GAC filter and the type of

carbon would need to be determined by the Manufacturer and FTO and approved by the State's pollution control authority. Since some SOC's are more readily adsorbed than others, and there may be competition between SOC's for adsorption sites on the carbon, GAC filters would have to be designed on a case-by-case basis. The discharge of treated water shall be directed to a location that is approved by the State.

#### **12.4 Analytical Schedule**

Feed water and treated water SOC samples shall be collected once per 25 hours of operation. Duplicate sampling is required for two of the samples of Verification Testing.

#### **12.5 Evaluation Criteria**

The difference in concentration of the SOC(s) of interest in the feed and treated waters will be compared to the Manufacturer's statement of performance for the equipment being tested. The ozone production and power usage may also be used to evaluate the performance of the equipment.

### **13.0 TASK 5: DATA MANAGEMENT**

#### **13.1 Introduction**

The data management system used in the Verification Testing program shall involve the use of computer spreadsheet software and manual recording of the operational parameters for the water treatment equipment on a daily basis.

#### **13.2 Experimental Objectives**

The objectives of this task are: 1) to establish a viable structure for the recording and transmission of field testing data so the FTO will provide sufficient and reliable operational data to the NSF for verification purposes, and 2) to provide the information needed for a statistical analysis of the data, as described in "Protocol for Equipment Verification Testing of Synthetic Organic Contamination Removal."

#### **13.3 Work Plan**

The following protocol has been developed for data handling and data verification by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases. Specific parcels of computer databases for operational and water quality parameters should then be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file. These specific database parcels will be identified based upon discrete time spans and monitoring parameters. In spreadsheet form the data will be manipulated into a convenient framework to allow analysis of water treatment equipment operation. Backup of the computer databases to diskette should be performed on a monthly basis at a minimum. When SCADA systems are not

available, direct instrument feed to data loggers and laptop computers shall be used when appropriate.

For parameters for which electronic data acquisition is not possible, field testing operators will record data and calculations by hand in laboratory notebooks (daily measurements will be recorded on specially-prepared data log sheets as appropriate). Each notebook must be permanently bound with consecutively numbered pages. Each notebook must indicate the starting and ending dates that apply to entries in the logbook. All pages will have appropriate headings to avoid entry omissions. All logbook entries must be made in black water insoluble ink. All corrections in any notebook shall be made by placing one line through the erroneous information. Products such as "correction fluids" are never to be utilized for making corrections to notebook entries. Pilot operating logs shall include a description of the water treatment equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items. The original notebooks will be stored on-site; photocopies will be forwarded to the project engineer of the FTO at an agreed upon schedule. This protocol will not only ease referencing the original data, but will also offer protection of the original record of results.

The database for the project will be set up in custom-designed spreadsheets. The spreadsheets will be capable of storing and manipulating each of the monitored water quality and operational parameters from each task, each sampling location, and each sampling time. All data from the laboratory notebooks and data log sheets will be entered into the appropriate spreadsheets. Data entry will be conducted on-site by the designated field testing operators. All recorded calculations will also be checked at this time. Following data entry, the spreadsheet will be printed out and the print-out will be checked against the handwritten data sheet. Any corrections will be noted on the hard-copies and corrected on the screen, and then a corrected version of the spreadsheet will be printed out. Each step of the verification process will be initialed by the field testing operator or engineer performing the entry or verification step.

Each experiment (e.g. verification run) will be assigned a run number which will then be tied to the data from that experiment through each step of data entry and analysis. As samples are collected and sent to state-certified or third party- or EPA-accredited laboratories, the data will be tracked by use of the same system of run numbers. Data from the outside laboratories will be received and reviewed by the field testing operator. These data will be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

### **13.4 Statistical Analysis**

Water quality developed from grab samples collected during test runs according to the Analytical Schedule in Task 2 of this Test Plan shall be analyzed for statistical uncertainty. The FTO shall calculate 95% confidence intervals for grab sample data obtained during Verification Testing as described in "Protocol for Equipment Verification Testing of Synthetic Organic Contamination Removal." Statistical analysis could be carried out for a large variety of testing conditions.

The statistics developed will be helpful in demonstrating the degree of reliability with which water treatment equipment can attain quality goals. Information on the differences in feed water quality variations for entire test runs versus the quality produced during the optimized portions of the runs would be useful in evaluating appropriate operating procedures.

## **14.0 TASK 6: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)**

### **14.1 Introduction**

Quality assurance and quality control of the operation of the water treatment equipment and the measured water quality parameters shall be maintained during the Verification Testing program.

### **14.2 Experimental Objectives**

The objective of this task is to maintain strict QA/QC methods and procedures during the ETV Program. Maintenance of strict QA/QC procedures is important in that if a question arises when analyzing or interpreting data collected for a given experiment, this information will be possible to verify exact conditions at the time of testing.

### **14.3 Work Plan**

Equipment flow rates and associated signals should be verified and verification recorded on a routine basis. Daily routine walk-throughs during the testing program will be used to verify that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to verify that chemicals are being fed at the defined flow rate, and into a flow stream that is operating at the expected flow rate. In addition, the operation of the air preparation equipment or the liquid oxygen supply for the ozone generator, and the ozone generator, shall be checked in each walkthrough and relevant operating data shall be recorded and checked to verify that operating conditions are within the acceptable operating range for the equipment or processes involved. In-line monitoring equipment such as flow meters, etc. will be checked as indicated below to verify that the readout matches with the actual measurement (i.e., flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

When collecting water quantity data, all system flow meters will be calibrated using the classic bucket and stopwatch method where appropriate. Hydraulic data collection will include the measurement of the finished water flow rate by the “bucket test” method. This would consist of filling a calibrated vessel to a known volume and measuring the time to fill the vessel with a stopwatch. This will allow for a direct check of the system flow measuring devices.

#### **14.3.1 Daily QA/QC Verifications**

- On-line turbidimeter: Clean out reservoirs and recalibrate, check the flow rate (verified volumetrically over a specific time period).
- On-line pH meters (standardize and recalibrate).
- Chemical feed pump flow rates (check and verify components).
- On-line turbidimeter readings checked against a properly calibrated bench model.

### **14.3.2 QA/QC Verifications Performed Every Two Weeks**

- On-line flow meters/rotameters: Clean equipment to remove any debris or biological buildup and verify flow volumetrically to avoid erroneous readings.
- Chemical feed pump flow rates (verify volumetrically over a specific period of time).

### **14.3.3 QA/QC Verifications Performed Every Testing Period**

- Tubing: Verify that all tubing and connections are in good condition and replace if necessary. For surface water systems, microbial growth could occur between seasonal verification test runs, so replacement of tubing prior to each verification test may be necessary.
- Differential pressure transmitters (verify gauge readings and electrical signals using a pressure meter).

## **14.4 On-Site Analytical Methods**

The analytical method utilized in this study for on-site monitoring of raw water and treated water quality are described in the following section. Use of either bench-top or in-line field analytical equipment will be acceptable for the verification testing; however, in-line equipment is recommended for ease of operation.

### **14.4.1 pH**

Analysis for pH shall be performed according to Standard Method 4500-H<sup>+</sup> B or EPA Method 150.1/150.2. A 2 point calibration of any pH meter used in this study will be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in poorly buffered waters. If this is a problem, measurement of pH in a confined vessel is recommended to minimize the effects of carbon dioxide loss with the atmosphere.

### **14.4.2 Turbidity Analysis**

Turbidity analyses shall be performed according to Standard Method 2130 or EPA Method 180.1 with either a bench-top or in-line turbidimeter. Grab samples shall be analyzed using a bench-top turbidimeter; readings from this instrument will serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of Verification Testing and on a weekly basis using primary turbidity standards of 0.1, 0.5 and 3.0 NTU. Secondary turbidity standards shall be used on a daily basis to verify calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.



During each verification testing period, the bench-top and in-line turbidimeters will be left on continuously. Once each turbidity measurement is complete, the unit will be switched back to its lowest setting. All glassware used for turbidity measurements will be cleaned and handled using lint-free tissues to prevent scratching. Sample vials will be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The Field Testing Organization shall be required to document any problems experienced with the monitoring turbidity instruments, and shall also be required to document any subsequent modifications or enhancements made to monitoring instruments.

**14.4.2.1 Bench-top Turbidimeters.** The method for collecting grab samples will consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity. When cold water samples cause the vial to fog and prevent accurate readings, allow the vial to warm up by submersing partially into a warm water bath for approximately 30 seconds.

**14.4.2.2 In-line turbidimeters.** In-line turbidimeters may be used during verification testing and must be calibrated as specified in the manufacturer's operation and maintenance manual. It will be necessary to periodically verify the in-line readings using a bench-top turbidimeter; although the mechanism of analysis is not identical between the two instruments the readings should be comparable. Should these readings suggest inaccurate readings then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic verification of the sample flow should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. It should also be verified that the LED readout matches the data recorded on the data acquisition system, if the latter is employed.

### **14.4.3 Dissolved Ozone**

The dissolved ozone concentration can be measured using an indigo bleaching technique, such as Standard Method 4500-O<sub>3</sub> B or the HACH Indigo AccuVac method. When sampling for dissolved ozone, it is important to minimize sample agitation and transfer from one container to another. One good sampling technique is to collect the sample directly from the sample tap. If HACH AccuVac vials are used, the tip of the AccuVac can be placed directly into the tap opening where the water is flowing. Apply pressure and snap the tip while it is inside the sample tap opening. The vacuum in the AccuVac vial will draw the water sample into the AccuVac. Once the AccuVac is filled, remove the AccuVac from the sample tap and analyze according the HACH instructions. If necessary, a short piece (i.e., less than 2 feet) of Tygon tubing can be attached to the sample tap for dissolved ozone sampling. If HACH AccuVac vials are not used, use of

tubing attached to the sample port for sample collection is recommended to minimize sample agitation and mixing. This tubing should be Tygon and should be no longer than 2 feet in length.

Another method for measuring dissolved ozone is a dissolved ozone probe. These probes can be placed in the process stream to provide continuous measurements of ozone residuals. Check the probe tip daily to ensure that the membrane has been installed properly and that there are no air bubbles underneath the membrane. Also, check that the pressure and flow rate within the contactor are within the appropriate range for the probe being used. The performance of the probe shall be verified on a daily basis by measuring the dissolved ozone concentration with one of the indigo bleaching methods to ensure that the probe is functioning properly.

A third method for measuring dissolved ozone concentrations is an on-line analyzer which uses UV spectrophotometry to measure the gas-phase concentration of ozone which has been stripped from a liquid sample. These analyzers then correlate the gas-phase ozone concentration to the dissolved ozone concentration. These analyzers are calibrated at the factory.

#### **14.4.4 Gas Phase Ozone**

Gas phase ozone concentrations can be measured using either UV absorbance ozone monitors or a wet-chemistry test. Ozone monitors are calibrated at the factory and provide a continuous measure of the ozone concentration in gas phase. The wet-chemistry test method of measuring the ozone concentration of a gas stream involves bubbling ozone through a potassium iodide solution, acidification with sulfuric acid, and titration with sodium thiosulfate. This method is described in detail in Gordon *et al.* (1992). During each Verification Test, a wet-chemistry measurement of the ozone feed gas shall be conducted to independently check that the ozone monitor is functioning properly. If ozone monitors are not available, wet-chemistry tests shall be performed three times per day or three times per shift to measure the ozone concentration in the feed gas and off gas.

#### **14.4.5 Hydrogen Peroxide**

The concentration of hydrogen peroxide can be measured using one of two spectrophotometric methods: 1) cobalt-bicarbonate and 2) peroxidase. The cobalt-bicarbonate method, described in Masschelein *et al.* (1977), can be used to measure up to 2 mg/L hydrogen peroxide at 260 nm, whereas the peroxidase method, described in Bader *et al.* (1988), can be used to measure up to 1.7 mg/L hydrogen peroxide at 551 nm.

At low pH, ozone and peroxide can be in solution at the same time, because the reaction rate is slow. The presence of ozone interferes with any hydrogen peroxide analysis; therefore, to measure the amount of hydrogen peroxide in the AOP system, ozone production shall be temporarily terminated while hydrogen peroxide samples are being collected and analyzed.

To ensure the proper feed rate of hydrogen peroxide to the ozone/AOP system, use a stopwatch to measure the time required to collect a specified volume of hydrogen peroxide stock solution from the feed system. This requires that the hydrogen peroxide feed line to the contactor be temporarily disconnected so that the pumping rate of the stock hydrogen peroxide solution can be measured. Typically, a graduated cylinder is used to collect the pumped hydrogen peroxide sample and the size of the graduated cylinder is such that the length of collection time exceeds 10 seconds.

The strength of the peroxide feed solution can also be determined from the peroxide supplier's shipping information, as long as the peroxide being used for testing has not been: 1) diluted by the user; 2) exposed to contamination (which would affect its strength); 3) stored for longer than one year; or, 4) stored at temperatures greater than 77° F.

#### **14.4.6 Temperature**

Readings for temperature shall be conducted in accordance with *Standard Method 2550*. Raw water temperatures shall be obtained at least once daily. The thermometer shall have a scale marked for every 0.1 °C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST). (A thermometer having a range of -1°C to +51°C, subdivided in 0.1° increments, would be appropriate for this work.)

#### **14.4.7 Color**

True color shall be measured with a spectrophotometer at 455 nm, using an adaptation of the *Standard Methods 2120* procedure. Samples shall be collected in clean plastic or glass bottles and analyzed as soon after collection as possible. If samples can not be analyzed immediately they shall be stored at 4°C for up to 24 hours, and then warmed to room temperature before analysis. The filtration system described in *Standard Methods 2120 C* shall be used, and results should be expressed in terms of PtCo color units.

#### **14.4.8 Dissolved Oxygen**

Analysis for dissolved oxygen shall be performed according to *Standard Method 4500-O* using an iodometric method or the membrane electrode method. The techniques described for sample collection must be followed very carefully to avoid causing changes in dissolved oxygen during the sampling event. Sampling for dissolved oxygen does not need to be coordinated with sampling for other water quality parameters, so dissolved oxygen samples should be taken at times when immediate analysis is going to be possible. This will eliminate problems that may be associated with holding samples for a period of time before the determination is made.

If the sampling probe is not mounted such that the probe is continuously exposed to the process stream, then care must be taken when measuring the dissolved oxygen concentration. For best results, collect the dissolved oxygen sample with minimal agitation and measure the dissolved oxygen concentration immediately. If possible,

measure the dissolved oxygen under a continuous stream of sample by placing the tip of the probe in the sample container, allowing the sample to overflow the container while the probe reaches equilibrium (usually less than 5 minutes).

## **14.5 Chemical and Biological Samples Shipped Off-Site for Analysis**

The analytical methods that shall be used during testing for chemical and biological samples that are shipped off-site for analyses are described in the section below.

### **14.5.1 Organic Samples**

Samples for analysis of total organic carbon (TOC), UV<sub>254</sub> absorbance, and dissolved organic carbon (DOC) shall be collected in glass bottles supplied by the state-certified or third party- or EPA-accredited laboratory and shipped at 4 °C to the analytical laboratory within 24 hours of sampling. These samples shall be preserved in accordance with Standard Method 5010 B. Storage time before analysis shall be minimized, according to Standard Methods.

### **14.5.2 Algae**

Algae samples shall be preserved with Lugol's solution after collection, stored and shipped in a cooler at a temperature of approximately 2 to 8 °C, and held at that temperature range until counted.

### **14.5.3 Inorganic Samples**

Inorganic chemical samples, including alkalinity, shall be collected and preserved in accordance with Standard Method 2320 B. The samples shall be refrigerated at approximately 2 to 8 °C. Samples shall be processed for analysis by a state-certified or third party- or EPA-accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 2 to 8 °C until initiation of analysis. Bromate samples shall be collected in sampling containers supplied by the state-certified or third party- or EPA-accredited laboratory. Sample collection and storage requirements are outlined in EPA Method 300.1 or shall be provided by the laboratory conducting the analysis.

### **14.5.4 SOC Analysis**

Analysis of SOC's requires a trained analyst using sophisticated instrumentation. Only state-certified or third party- or EPA-accredited laboratories shall analyze SOC samples that are collected during Initial Operations and Verification Testing. As stated in the "Protocol for Equipment Verification Testing of Synthetic Organic Contamination Removal," approved methods for some SOC's may not be available, and for these SOC's, a proposed, peer-reviewed method may be used.

There are many approved methods for analyzing Phase II and Phase V SOC's. Depending on the laboratory, gas chromatography (GC) or high performance liquid chromatography

(HPLC) methods can be used to analyze SOC<sub>s</sub>. For both methods, the equipment is highly specialized and proper operation of these instruments requires a skilled laboratory technician.

Mass spectrometry is not required for all SOC<sub>s</sub>, however it is recommended for SOC identification. Retention times relative to the internal standard can also be used to identify SOC<sub>s</sub>. Either peak height or peak area can be used to determine the SOC concentrations.

SOC<sub>s</sub> shall be analyzed with an internal standard similar in analytical behavior and not affected by the matrix for QA/QC. An appropriate surrogate standard shall also be used during SOC analysis. Data pertaining to the internal and surrogate standards shall be reported with the SOC concentrations of the samples being analyzed. A method blank shall also be prepared and analyzed by the state-certified or third party- or EPA-accredited laboratory to verify minimal contamination in the laboratory.

At least three standards shall be used to develop the standard curve for SOC quantification and these three standards shall be extracted and analyzed (by GC or HPLC) on the same day as the samples.

During each Verification Test period, one treated water sample shall be analyzed by scanning for the presence and concentration of potential by-products of SOC oxidation by ozone. Gas chromatography followed by mass spectrometry can be used to identify many of the organic by-products formed by ozonation. The spectra obtained by this analysis can be matched to a compound library in a computer database to identify the various byproducts. This analysis shall be performed by a state-certified or third party- or EPA-accredited analytical laboratory. The scan should be targeted toward the SOC of interest, and the potential by-products associated with ozonation of that SOC.

Spiked samples shall be analyzed once, at the beginning of each Verification Test Run. The laboratory shall spike a feed water sample with a known quantity of the SOC(s) of interest and analyze this spiked sample. SOC analysis of the spiked sample will indicate if there are any interferences present in the feed water. The broad scan can be a performance-based scan (i.e., the scan is not used for compliance, and therefore undergoes less rigorous QA/QC and is less expensive than a compliance based scan analysis.)

## **14.6 Experimental QA/QC Samples**

### **14.6.1 Process Control**

A second round of testing shall be carried out using procedures identical to the steps outlined above, but without operating the ozone or ozone/AOP equipment. The purpose of this testing is to evaluate any cumulative effects produced by the package plant, the spiking and sampling procedures, and the sample handling procedures on SOC<sub>s</sub>. The process control samples should show minimal loss of SOC(s) relative to the trip control sample. Significant loss of SOC concentrations in the process control sample indicates that some aspect of the process other than ozone oxidation contributes to SOC removal. Re-testing is required when this is shown to occur.

#### **14.6.2 Trip Control**

For tests utilizing spiked SOC(s), a replicate or subsample of the spiking solution shall accompany the actual spiking solution from the analytical laboratory. This replicate sample shall undergo all of the processes used on the actual solution including dose preparation, shipping, preparation for spiking, and return to the laboratory for analysis. The trip control samples should show minimal loss of SOC(s). Significant decreases in the SOC concentration of the trip control sample indicates that some step in handling the solution contributed to the reduction in the SOC concentration. The seeding tests must be repeated when significant loss of SOC(s) in the trip control sample is observed.

### **15.0 OPERATION AND MAINTENANCE**

The FTO shall obtain the Manufacturer-supplied Operation and Maintenance (O&M) Manual to evaluate the instructions and procedures for their applicability during the verification testing period. The following are recommendations for criteria for O&M Manuals for package drinking water treatment equipment employing ozone treatment.

#### **15.1 Maintenance**

The Manufacturer shall provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment including, but not limited to, the following, where applicable:

- ozone generator (dielectric replacement)
- ozone diffusers or injection port, control valves
- ozone destruct unit (catalyst replacement)
- gas phase ozone monitors (for feed gas and off gas)
- dissolved ozone monitoring equipment
- cooling water equipment
- air preparation unit or oxygen feed system for ozone generation
- gas and liquid rotameters
- UV lamps and other relevant equipment
- peroxide feed equipment
- other equipment such as pumps and valves

The Manufacturer shall also provide readily understood information on the recommended or required maintenance for non-mechanical or non-electrical equipment, including but not limited to, the following, where applicable:

- piping
- contactor chamber

## 15.2 Operation

The Manufacturer shall provide readily understood recommendations for procedures related to proper operation of all package plant equipment. Among the operating aspects that should be addressed in the O&M manual are:

### Ozone Generator

- air preparation or oxygen feed requirements (moisture content, filtration requirements, flow rate)
- cooling water requirements (flow)
- range of variable voltage for adjusting ozone output
- proper sequence of operation for start-up and shut-down
- proper sequence of operation for initial start-up or for re-start after maintenance

### Ozone Monitors (Gas Phase)

- temperature and pressure compensation
- zeroing and calibration procedures
- proper sequence of operation for start-up and shut-down

### Ozone Destruct Units

- heater and/or blower requirements
- catalyst requirements
- proper sequence of operation for start-up and shut-down

### Air Preparation or Oxygen Feed Systems

- desiccant requirements and replacement procedures
- filters (maintenance and replacement schedule)
- proper sequence of operation for start-up and shut-down
- supplemental gas (air or nitrogen) flow rate, pressure, and temperature.

### Cooling Water System

- maintenance of proper temperature
- monitoring cooling water flow
- pump maintenance
- proper sequence of operation for start-up and shut-down
- maintenance of recirculation equipment, if cooling water is recirculated

### Ozone Contactor Systems

- maintenance schedule and procedures
- replacement procedures

### UV lamps

- hours of operation (verification procedures)
- UV irradiance (calibration and verification procedures)
- maintenance schedule and procedures
- replacement procedures
- proper sequence of operation for start-up and shut-down

### Hydrogen Peroxide Feed System

- procedures for variable speed adjustments to pump
- information about proper tubing type and size
- anticipated schedule for tubing replacement
- storage information (i.e., safety, container type, container material, temperature, length of storage time) for stock hydrogen peroxide solutions
- proper sequence of operation for start-up and shut-down

### Control Valves

- open/close indication
- sequence of operations

The Manufacturer shall provide a troubleshooting guide; a simple checklist of what to do for a variety of problems, including but not limited to:

- no flow to unit
- sudden change in flow to unit
- no electric power
- automatic operation (if provided) not functioning
- valve stuck or will not operate

## 16.0 REFERENCES

APHA, AWWA, and WEF (1995). *Standard Methods for the Examination of Water And Wastewater*, 19th Ed., APHA, Washington, DC.

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**Table 1. Water Quality Sampling and Measurement Schedule**

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	Groundwater Systems
Temperature (°C)	Feed water and Treated Water	M	3/d or 3/shift	3/d or 3/shift
Dissolved Ozone Residual (mg/L)	Treated†	O	3/d or 3/shift	3/d or 3/shift
pH	Feed Water	M	3/d or 3/shift	3/d or 3/shift
Total Alkalinity (mg/L as CaCO <sub>3</sub> )	Feed Water	O	1/d	1/d
Total Organic Carbon (mg/L)	Feed Water	O	1/25 hours of ozone production	1/50 hours of ozone production
Dissolved Organic Carbon (mg/L)	Feed Water	O	1/25 hours of ozone production	1/50 hours of ozone production
UV absorbance at 254 nm (1/m)	Feed Water, Treated water	O	1/d	1/50 hours of ozone production
Color (Pt-Co)	Feed Water, Treated water	O	1/d	1/50 hours of ozone production
Turbidity (NTU)	Feed Water, treated water	O	3/d or 3/shift	1/d
Bromide (mg/L)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production

**Table 1. Water Quality Sampling and Measurement Schedule (continued)**

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	Groundwater Systems
Bromate (µg/L)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
SOCs (µg/L)	Feed Water, Treated water	M	1 per 25 hours of ozone production	1 per 25 hours of ozone production
SOC scan	Treated Water Feed Water	M	1 per Verification test period, after 100 <sup>th</sup> hour of operation	1 per Verification test period, after 100 <sup>th</sup> hour of operation
Total THM (µg/L) (chloroform, bromoform, bromodichloromethane, dibromochloromethane)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
HAA <sub>5</sub> (µg/L) (monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid, trichloroacetic acid)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Iron (µg/L)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Dissolved Manganese (µg/L) (Manganese concentration passing through 0.2 µm filter)	Feed Water Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Total Manganese (µg/L)	Feed Water Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production

**Table 1. Water Quality Sampling and Measurement Schedule (continued)**

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	Groundwater Systems
Total Sulfides	Feed Water	O	1/d	1/d
Dissolved Oxygen	Feed Water Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Hydrogen Peroxide (mg/L)	Stock Solution Treated Water	M††	1/50 hours of ozone production 1/Verification Test Period	1/50 hours of ozone production 1/Verification Test Period
Quenching Solution (mg/L) (e.g., hydrogen peroxide)	Feed Water	M	1/d	1/d
Algal enumeration and species	Feed Water	O	1 per Verification Test Period	Not Required
Calcium (mg/L as CaCO <sub>3</sub> )	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Total Hardness (mg/L as CaCO <sub>3</sub> )	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production

\* 3/d or 3/shift means that the water quality parameter shall be measured either 3 times per day if ozone production is continuous over the 200 hours of Verification Testing, or 3 times per staffed shift if ozone production is periodically terminated or interrupted, and the length of time of ozone production is less than 24 hours. 1/50 hours of ozone production means that the water quality parameter shall be measured once per each 50 hours of ozone production, regardless of interruptions in ozone production. † The dissolved ozone concentration should be measured at sampling ports within the ozone contactor or immediately at the outlet of the ozone contactor. If the ozone decay coefficient is being determined, at least two sampling ports will need to be sampled. †† The peroxide concentration of the stock solution shall be checked at the prescribed frequency. The peroxide concentration within the contactor shall be checked once during or immediately prior to the verification testing period, while the ozone equipment is not operating. Peroxide monitoring within the contactor will require that samples be withdrawn at appropriate sampling ports at the end or outlet of the contactor.

**Table 2. Analytical Methods**

Parameter	Facility	<i>Standard Methods</i> number or Alternative Reference <sup>1</sup>	EPA Method <sup>2</sup>
Temperature (°C)	On-site	2550 B	
Dissolved Ozone Residual (mg/L)	On-site	4500 O <sub>3</sub> B; HACH Indigo Blue Method*	
pH	On-site	4500 H <sup>+</sup>	150.1/150.2
Total Alkalinity (mg/L as CaCO <sub>3</sub> )	Lab	2320 B	
Phase II and Phase V SOCs	Lab	6252, 6410, 6420, 6431, 6440, 6610, 6630, 6640, 6651	525.2, 505, 515.1, 531.1, 547, 548.1, 549.1, 1613
Total Organic Carbon (mg/L)	Lab	5310 C	
Dissolved Organic Carbon (mg/L)	Lab	5310 C	
UV absorbance at 254 nm (1/m)	Lab	5910 B	
Color (Pt-Co)	Lab	2120 C	110.2
Turbidity (NTU)	On-site	2130 B	180.1
Bromide (mg/L)	Lab	4500-Br <sup>-</sup>	300.0
Bromate (µg/L)	Lab		300.1
Total THM (µg/L)	Lab	6232 B	502.2, 524.2, 551
HAA <sub>5</sub> (µg/L)	Lab	6251 B	552.1
Iron (µg/L)	Lab	3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9
Total Manganese (µg/L)	Lab	3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9
Dissolved Manganese (µg/L) (Manganese concentration passing through 0.2 µm filter)	Lab	3500-Mn	3111 B, 3113 B, 3120 B
Total Sulfides	Lab or On-Site	4500-S <sup>2-</sup> D, E	
Dissolved Oxygen	Lab or On-Site	4500-O	

**Table 2. Analytical Methods (continued)**

Parameter	Facility	<i>Standard Methods</i> number or Alternative Reference <sup>1</sup>	EPA Method <sup>2</sup>
Algal enumeration and speciation	Lab	Part 10000, Biological Examination†	
Calcium (mg/L as CaCO <sub>3</sub> )	Lab	3500-Ca D, 3111 B, 3120 B	200.7
Total Hardness (mg/L as CaCO <sub>3</sub> )	Lab	2340 C	
SOC scan	Lab	6410B, 6420C, 6440C	525.2 – Extended for Broad Spectrum

\* Dissolved ozone residual measurements can also be from a properly calibrated and installed dissolved ozone monitor or properly calibrated and installed dissolved ozone monitor.

† *Standard Methods* does not contain a method for enumeration and speciation of algae. It does, however, contain methods for laboratory techniques that may need to be performed for proper enumeration and speciation of the algae. Only an experienced and qualified laboratory analyst shall conduct algal enumeration and speciation.

<sup>1</sup> Standard Method Source: 19th Edition of *Standard Methods for the Examination of Water and Wastewater*, 1995, American Water Works Association.

<sup>2</sup> EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

**Table 3. Package Treatment Plant Operating Data**

Operational Parameter		Frequency
Water Flow (gpm)	Feed Water	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
	Cooling Water	3/d or 3/shift
Water Pressure (psig)	Inlet to Ozone System	3/d or 3/shift
	Outlet of Ozone System	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
	Cooling Water	3/d or 3/shift
Water Temperature (°C)	Inlet to Ozone System	3/d or 3/shift
	Outlet of Ozone System	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
Gas Phase Ozone Concentration (% wt)	Feed Gas	3/d or 3/shift
	Off Gas	3/d or 3/shift
Power Usage (kw/hr)	Ozone Generator	3/d or 3/shift
	Air Preparation System or Oxygen System	3/d or 3/shift
	Gas Phase Ozone Feed and Off Gas Monitors	3/d or 3/shift
	Cooling Water System	3/d or 3/shift
	Destruct Units	3/d or 3/shift
	Other pumps or motors	3/d or 3/shift
Ozone Feed Gas Temperature (°C)		3/d or 3/shift
Ozone Feed Gas Pressure (psig)		3/d or 3/shift
Ozone Feed Gas Flow (scfm)		3/d or 3/shift
Atmospheric Pressure (psia)		1/d
Dew Point (if using air feed system)		1/d
Ozone Production (lb/d)		1/d
Ozone Decay Rate (1/minute) (optional)		1/d
If applicable: Peroxide feed concentration (mg/L) Peroxide feed rate (mL/min) Peroxide to Ozone ratio (by weight)		3/d or 3/shift
If applicable: Purity of oxygen supply (%) Supplemental nitrogen flow rate (scfm), pressure (psig), and temperature (°C) Supplemental air flow rate (scfm), pressure (psig), and temperature (°C)		1/d or 1/shift 1/d or 1/shift 1/d or 1/shift
If applicable: Operating parameters for UV-light systems (see NSF Equipment Verification Testing Plan for Microorganism Contaminant Inactivation by Ultraviolet Based Technology Used in Packaged Drinking Water Treatment Systems For Small Public or Private Water Supplies)		3/d or 3/shift